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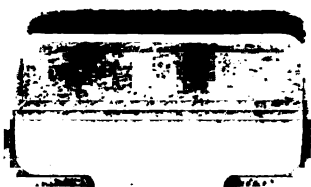
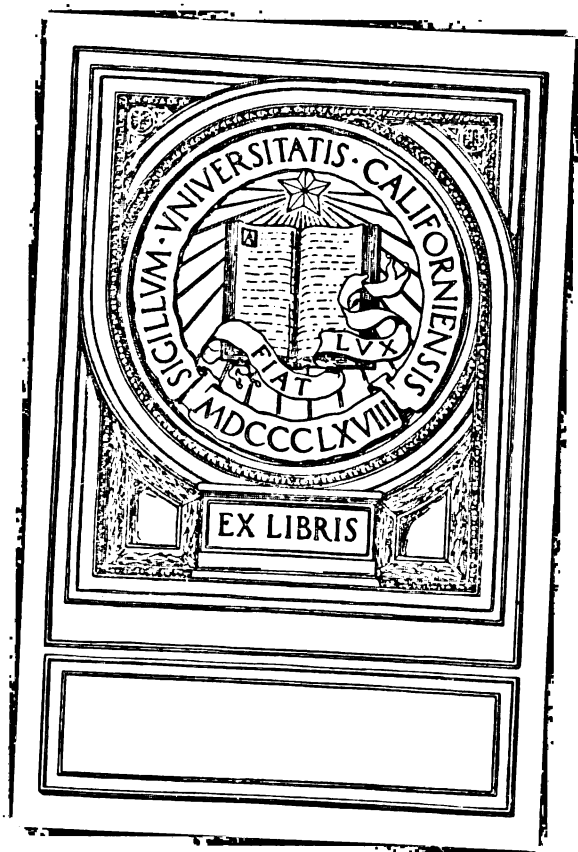
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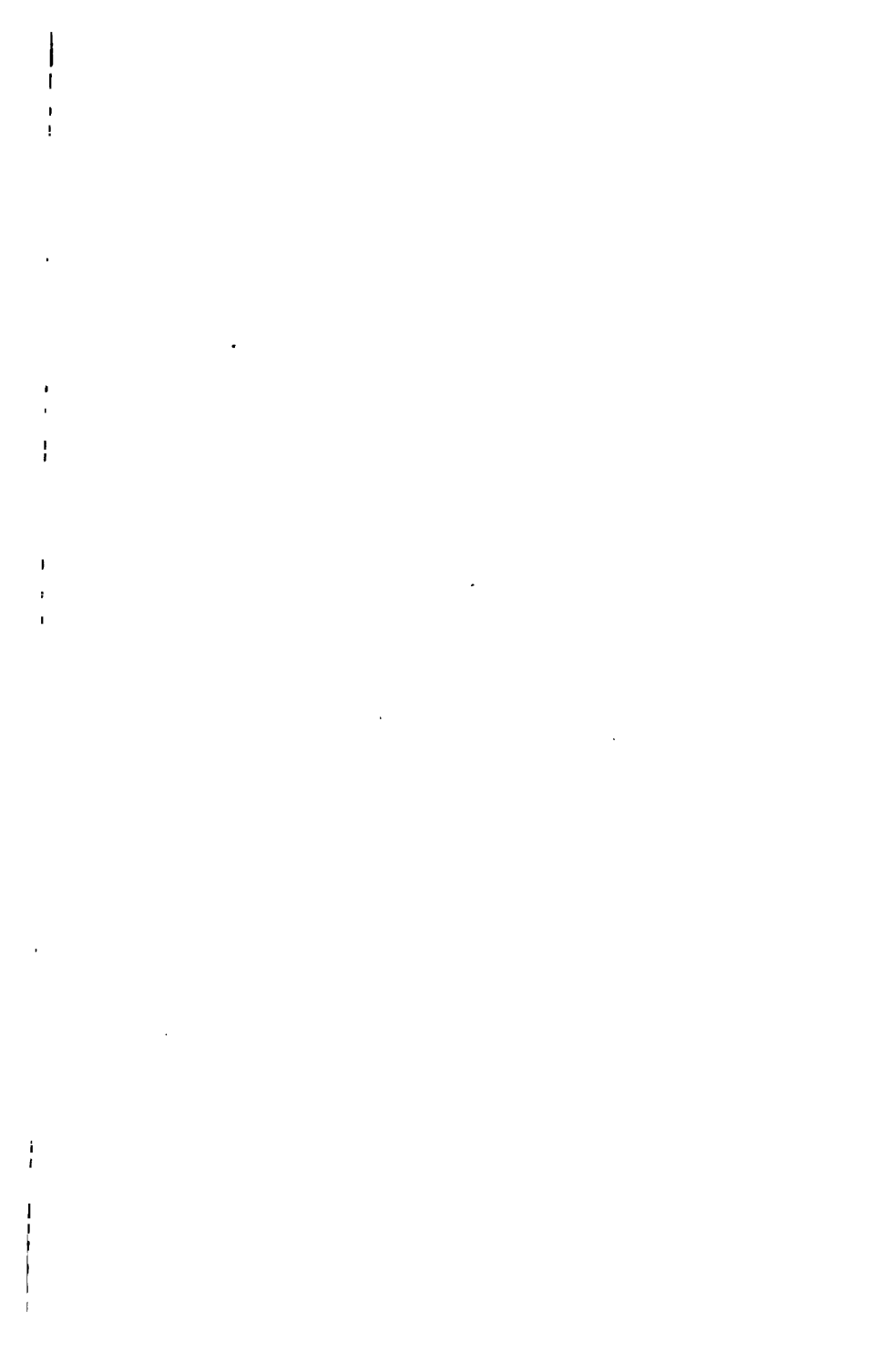
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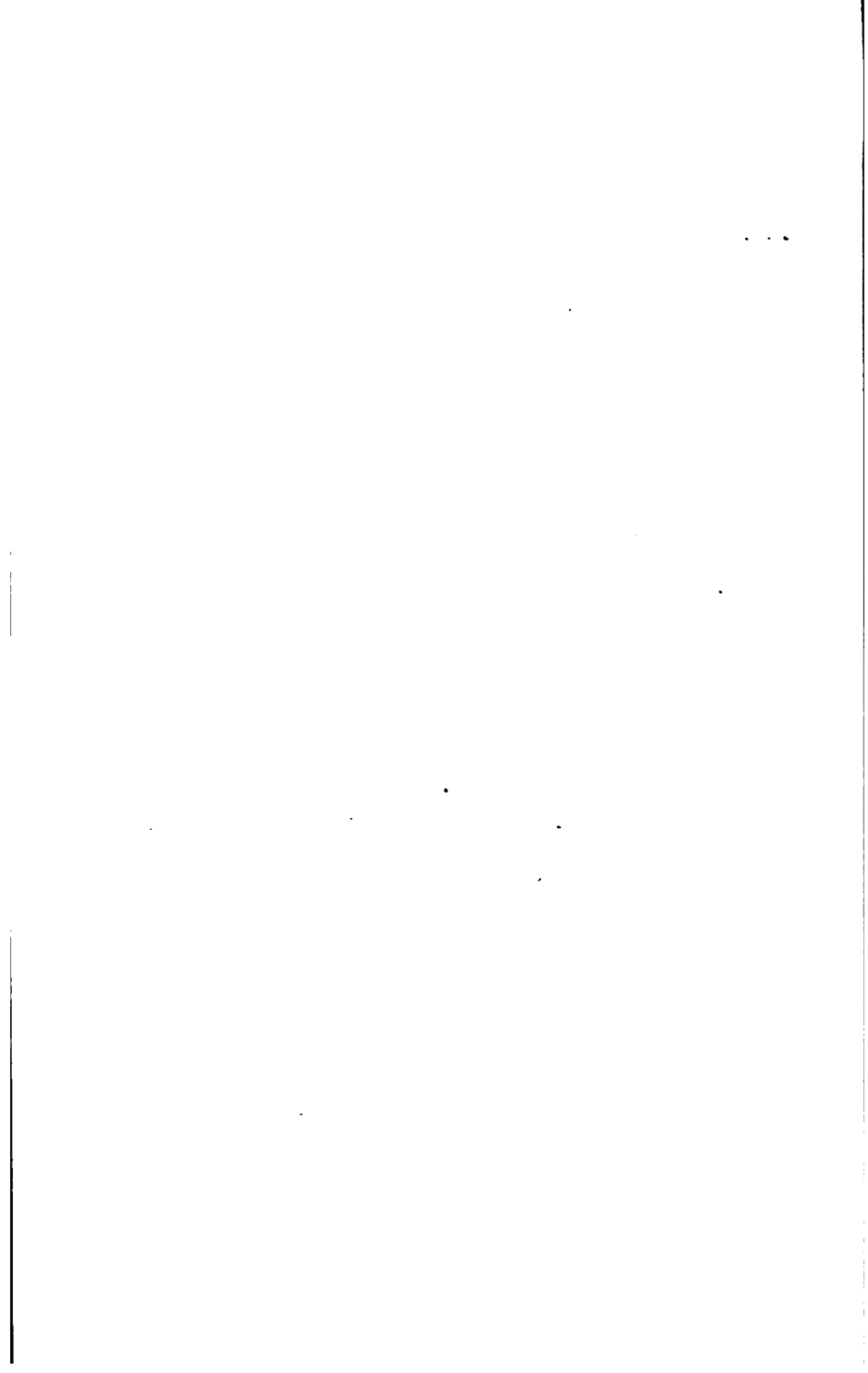
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**AN INTRODUCTION TO THE STUDY
OF
METALLURGY.**

NEW METALLURGICAL SERIES

EDITED BY

W. C. ROBERTS-AUSTEN, C.B., F.R.S.,

Chemist and Assayer of the Royal Mint ; Professor of Metallurgy in the
Royal College of Science.

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11

12

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14

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16

17

18

AN INTRODUCTION TO THE STUDY
OF
METALLURGY.

BY

W. C. ROBERTS-AUSTEN, C.B., F.R.S.,
ASSOCIATE OF THE ROYAL SCHOOL OF MINES; CHEMIST AND ASSAYER OF THE ROYAL MINT;
PROFESSOR OF METALLURGY IN THE ROYAL COLLEGE OF SCIENCE, WITH WHICH
THE ROYAL SCHOOL OF MINES IS INCORPORATED.

THIRD EDITION, REVISED AND ENLARGED.

ONE OF A SERIES OF TREATISES WRITTEN BY
ASSOCIATES OF
THE ROYAL SCHOOL OF MINES.

LONDON:
CHARLES GRIFFIN & COMPANY, LIMITED,
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1894.

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"I rather open, than discover things."

MONTAIGNE'S ESSAYS (1580).

"To know

Rather consists in opening out a way
Whence the imprisoned splendour may escape,
Than in effecting entry for a light
Supposed to be without."

BROWNING'S "PARACELUS" (1835).

TO VINU
ADPOTUAO

TO THE
HON. SIR C. W. FREMANTLE, K.C.B.
DEPUTY-MASTER OF THE MINT.

FOR more than twenty years there have been few things, except this dedication, about which I have not consulted you. The book embodies the results of many investigations conducted in the Mint during that period, and the encouragement you have always given to research, and your interest in its progress, have been most helpful. This is, however, only one of the many reasons why this slender gift is so gladly offered to you, as it is now, with the sincere friendship of

THE AUTHOR.

PREFACE TO THE THIRD EDITION.

THE Author is much gratified to find that the effort made in the earlier editions of this book to afford a basis for the study of Metallurgy by systematically arranging facts connected with metals and with their extraction from the ore has been welcomed by students, by practical metallurgists, and by chemists. In the present edition the scope of the work has been extended, and a hundred new pages have been added to the volume. The growing importance of Molecular Mechanics in relation to Metallurgical problems, has rendered it necessary to insert a new chapter on Thermochemistry. A special chapter has also been added in which the mode of studying the micro-structure of metals and alloys is dealt with. Large additions would have been made to the portion which relates to alloys, but it was considered better that a special treatise should be devoted to them. This is in an advanced stage of preparation, and, with the series of treatises which are being written under the Author's guidance, for the most part by Associates of the Royal School of Mines who have special knowledge of individual metals, will, it is hoped, serve to make the literature of Metallurgy adequately represent the progress which has been made in recent years.

March, 1894.

PREFACE.

THE literature of metallurgy is rich, but those who are beginning to study it need guidance to a knowledge of the principles on which the art is rightly practised. It depends, as is well known, on the application of chemistry, physics, and mechanics; but the methods of metallurgists vary greatly from those of chemists, who, however, frequently fail to appreciate the nature of the difference.

Ten years' experience has convinced me that it is more important at the outset for the student to know what was the scope of mind of the early practisers of metallurgy, and to see what kind of aid the art may be expected to receive in future from the sciences, than to acquire familiarity with complicated details of processes and appliances. In this little volume I have, therefore, devoted four chapters to these branches of the subject, embodying in them portions of lectures which I have delivered from time to time.

In all English works on metallurgy, the important metals are dealt with separately and in detail. In this, however, an attempt has been made to treat the subject as a whole, giving no minute descriptions of processes, but choosing typical appliances and indicating their use in connection with groups of metals. Such a method was adopted by the late M. Gruner, Professor of Metallurgy at the *École des Mines*, Paris, to whom I have reason to be grateful, for I have closely followed him in my class lectures.

The student will, I trust, be led to study the works in which

the extraction of metals from their ores and fitting them for use are fully discussed. Such are the classical treatises of Percy, the monographs of Sir Lowthian Bell, and the manual of Phillips and Bauerman, from which volume a few illustrations have been borrowed. The literature of the subject has been enriched by Howe, of Boston, who has collected a store of facts in his elaborate and recently-published volume on steel.

In the preparation of a portion of this little work, I have been aided by my colleague, Mr. Bennett Brough, whose help has been specially useful in passing the work through the press.

I hope that the book will be found useful to my own students, for whose progress I feel sincere solicitude.

CHILWORTH, SURREY,

December 23, 1890.

CONTENTS.



CHAPTER I

THE RELATION OF METALLURGY TO CHEMISTRY.

CHAPTER II.

PHYSICAL PROPERTIES OF METALS.

	PAGE
Molecular structure	7
Density	8
Fracture	9
Malleability	10
Ductility	10
Tenacity	10
Toughness	10
Hardness	10
Brittleness	11
Elasticity, extensibility, and strength of metals	11
Influence of foreign elements on the strength of metals	20
Colour	33
Fusibility	33
Welding	34
Properties common to fluids and solid metals	35
Occlusion of gases	45
Table of physical constants of metals	48

CHAPTER III.

ALLOYS.

Early investigations	51
Views as to the constitution of alloys	52
Union of metals by fusion	55
" compression	56
" electro-deposition	59

	PAGE
Liquation	59
Action of electric currents on molten alloys	65
Conduction of electricity by alloys at high temperature	67
Allotropic modifications of metals resulting from alloying	70
Influence of varying quantities of metals on each other	76
Colour of alloys	83
Alloys of industrial importance	87

CHAPTER IV.

THE THERMAL TREATMENT OF METALS.

Annealing, hardening, and tempering	91
History	93
Internal constitution of steel	95
Working of steel	112
Classification of steel	116
Summary	118

CHAPTER V.

FUEL AND THERMAL MEASUREMENTS.

Classification of fuel	139
Calorific power	140
Calorific intensity	141
Pyrometry	142
General considerations	166
Experimental work	169
I.—Natural fuels	178
(1) Wood	178
(2) Peat	179
(3) Lignite	180
(4) Coal	181
(5) Anthracite	183
(6) Liquid fuels	184
(7) Natural gas	185
II.—Prepared fuels	186
(1) Compressed fuels	186
(2) Dried fuels	186
(3) Carbonised fuels	186
(a) Charcoal	186
(b) Coke	188
(4) Gaseous fuel	198
Water Gas	202
Bibliography	203

CONTENTS.

XV

CHAPTER VI.

MATERIALS AND PRODUCTS OF METALLURGICAL PROCESSES.

	PAGE
Ores	204
Fluxes	204
Metallurgical agents	205
Selection of fluxes	206
Slags	206
Economic application of slags	208
Calculation of furnace charges	210
Classification of metallurgical operations	220
Roasting and calcination	222
Oxidising agents	223
Reducing agents	224
Chemical agents	225

CHAPTER VII.

FURNACES.

Materials used in the construction of furnaces	227
Crucibles	229
Classification of furnaces	230
(1) Hearths	233
(2) Shaft furnaces	237
(3) Reverberatory furnaces	255
(4) Closed-vessel furnaces	267
The Bessemer converter	269

CHAPTER VIII.

MEANS OF SUPPLYING AIR TO FURNACES.

Means of producing draught	277
Blowing engines	281
Hot-blast stoves	282

CHAPTER IX.

THERMO-CHEMISTRY.

Units	289
Bomb calorimeter	290
Chemical equilibrium	294
Thermal equations	298
Bibliography	312
<i>Folding Table to face</i>	312

CHAPTER X.

TYPICAL METALLURGICAL PROCESSES.

	PAGE
Classification of processes	313
Welsh method of copper smelting	316
Smelting of gold and silver ores in Colorado	320
Freiberg process	323
Wet processes for treating argentiferous copper ores	340
Chlorination of gold ores	342
Purification of platinum	344
Wet process for treating nickel and cobalt ores	345
System of teaching metallurgy	348

CHAPTER XI.

THE MICRO-STRUCTURE OF METALS AND ALLOYS.

History	351
Preparation of specimens	352
Illumination	353
Bibliography	356

CHAPTER XII.

ECONOMIC CONSIDERATIONS.

Object of the metallurgist	359
Capital and labour	359
Production of metals	367
Price of metals	368
Conclusion	371

INDEX	373
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INTRODUCTION TO THE STUDY OF METALLURGY.

CHAPTER I.

THE RELATION OF METALLURGY TO CHEMISTRY.

THE distinguished metallurgist who may be said to have created the English literature of the subject concluded the introductory lecture he delivered* at the Royal School of Mines, by pointing out to the students who were then beginning their course, that "in proportion to the success with which the metallurgic art is practised in this country, will the interests of the whole population, directly or indirectly, in no inconsiderable degree, be promoted."

During the period of more than forty years since Dr. Percy began to teach, the conditions under which metallurgy is practised have changed considerably; for the field of knowledge has so widely extended, the scale on which operations are conducted is now so great, and the mechanical appliances they involve are so varied and complicated, that while the interest of the subject is deepened, its difficulty is gravely increased. Metallurgy involves not only a knowledge of "the art of extracting metals from their ores," but also of the means of "adapting them for use," which is effected by complicated mechanical operations, and, strange as it may seem, by varying the degree of purity, often to a very slight extent. It will thus be evident that the student must possess adequate knowledge of Inorganic Chemistry, Mechanics, and Physics. Besides this, he must acquire aptitude for dealing with economic details.

* *Records of the School of Mines*, vol. i. pt. i. (1852), p. 127

Historical Sketch.—In turning to the history of metallurgy, it is easy to be led away by the charm of the antiquarian store of riches into devoting too much time to literary research. It should be remembered, however, that much of what is both interesting and full of suggestion, even at the present day, is to be found buried in the treatises by the old writers whose work we inherit and continue.

Primitive metallurgical processes are referred to in some of the oldest known historical records; naturally, therefore, the scientific development of metallurgy must have been long preceded by its empirical practice as an art, an art for which a place has even been claimed among the religious systems of antiquity.* The earlier literature of the subject consists mainly of descriptions of processes; but it is well known that chemistry was to a great extent built up on a metallurgical basis, and Black's singularly advanced definition of chemistry as the "effects produced by heat and mixture"† might well be applied to metallurgy. The library of Leyden contains a papyrus which has been described by M. Reuvens,‡ and which is considered by Kopp§ to be the oldest known chemical manuscript, its date being possibly as early as A.D. 200. It treats generally of metallurgical matters, and the purification of gold and silver is frequently mentioned. Of all chemical phenomena, probably none have more contributed to advance chemistry as a science than those bearing upon the relations between oxygen and lead; and the interest attaching to the mutual behaviour of these two elements is so great that the student will do well to consider the influence of one very ancient metallurgical process on the scientific views of the present day.

When lead is melted with free access of air, a readily fusible substance forms on its surface. This substance may be allowed to flow away, or, if the metal is contained in a suitable porous receptacle, the fusible oxide sinks into this containing vessel; in either case the oxidation of the lead affords a means of separating it from precious or inoxidisable metals, if any were originally present in the lead. The above fact has been known from remote antiquity, and the early Jewish writers allude to it as old and well-known. They clearly show, for instance, that lead can be removed from silver by being "consumed of the fire," while the silver is not affected. That the Greeks knew and practised this

* Rossignol, *Les Métaux de l'Antiquité* (1863).

† *Lectures*. By Joseph Black, M.D., vol. i. pp. 11, 12 (Edin. 1803).

‡ Reuvens, *Lettres à M. Letronne* (Leyden, 1830), quoted by Prof. Ferguson in an address to the Glasgow Phil. Soc. (1876), p. 19.

§ *Beiträge zur Geschichte der Chemie*, 1869.

method of *cupellation* is abundantly proved, if only by certain specimens of gold and silver which were discovered by Dr. Schliemann on the site of ancient Troy. The Arabians investigated the subject, as is shown by the writings of Geber,* the greatest of the early chemists (he died in 777), who gives a remarkable account of cupellation; he also describes the conversion of lead into a fine powder by calcination with much clearness, and he noticed the fact that after calcination the mass has "acquired a new weight in the operation." His subsequent observations on the reduction of altered metals from their "calxes" show that he knew the weight to be increased; in any case it is interesting to remember that his work was, in a sense, quantitative. He, moreover, was cognisant of the fact that two different substances may be produced by heating lead in air, and he assumed that "in the fire of calcination a fugitive and inflammable substance is abolished." The alchemists refer continually to the subject, and "deliver themselves," as Roger Bacon said, in his *Speculum Alchimie*, "in the enigmas and riddles with which they clouded and left shadowed to us the most noble science." Eck of Sulzbach showed (1489) that metals augment in weight by calcination, and that what we now call red oxide of mercury gives off "a spirit" when heated; had he named and isolated the spirit, he would have discovered oxygen. The great metallurgist of the sixteenth century, Agricola,† points out that lead increases in weight when it is exposed to the action of moist air. In the middle of the sixteenth century, the equally accomplished metallurgist, Biringuccio,‡ contemporary of Paracelsus and Agricola, seems to have been specially attracted by the phenomenon in question, and he remarks:—"If we had not lead we should work in vain for the precious metals, for without its aid we could not extract gold or silver from the stones containing them. . . . The alchemists also," he says, "make use of it in their operations, calcining it by itself or with other substances; but," he goes on to observe, "the calcination, conducted in a reverberatory furnace is accompanied by a marvellous effect, the result of which should not be passed by in silence, for lead thus treated increases ten per cent. in weight, and considering that most things are consumed in the fire, it is remarkable that the weight of lead is increased and not diminished." Although he subsequently gives evidence of much accurate know-

* The works of Geber, translated by R. Russell (1686), pp. 74, 78, 220,

234.

† *De ortu et causis subterraneorum*, p. 519.

‡ *Pirotechnia* (Vinezia, 1540), translated into French by T. Vincent (Rouen, 1627), p. 41.

ledge of practical metallurgy, his views as to this particular phenomenon were hardly in advance of Geber's; but we may claim Biringuccio as an early metallurgist, who knew the facts and recognised that they were theoretically important. Cæsalpinus, in his work, *De Metallicis*, showed that the film which covers lead exposed to moist air and augments its weight, is due to an aëriform body. It was not till nearly a century later (1630) that a French chemist, Jean Rey,* stated that the increase in weight came from the air. The problem attracted much attention in England, and it is not a little interesting that among the very first experiments recorded by our own Royal Society, is a metallurgical series relating to the weight of lead increased in the fire on the "copels" at the assay office in the Tower, the account being brought in by Lord Brouncker in February, 1661.† Subsequently, in 1669, John Mayo showed that the increase in weight of calcined metals was due to a "spiritus," or distinct constituent of ordinary air.‡ Nevertheless, Boyle heated lead in a small retort,§ and attributed the increase in weight, as Lemery also did,|| to his having "arrested and weighed igneous corpuscles." One of the most curious passages known is in the *Hippocrates Chemicus* of Otto Tachen, a German who lived at Venice, and published his book there in 1666. He describes how lead, when burnt to minium, increases in weight. This increase he ascribes to a substance of acid character in the wood used for burning, and then, by a very ingenious course of argument, based on the saponifying powers of litharge, makes out that lead is of the nature of, or contains an alkali which combines with, the "occult acid of the fat." This is a curious anticipation of a very modern classification, which brings lead into relationship with the alkalies and alkaline earths, as well as of Chevreul's investigations on saponification. Cæsalpinus had previously called lead "a soap" which in cupellation washes gold and silver.

It is hardly necessary to point out how important this calcination of lead was considered by those who defended the Phlogistic theory in regard to chemical change, the theory propounded by the metallurgist Becker, which, for more than a century, exerted so profound an influence on scientific thought. His views were first embodied in the *Physica Subterranea* (1669) and in the *Alphabetum Minerale* (1682).

* *Essais de Jean Rey* (reprinted in Paris, 1777), p. 64.

† MS. register book of the Royal Society.

‡ *Tractatus quinque Medico-Physici*, p. 25 et seq. (Oxonii, 1674).

§ Collected works, vol. ii. (1744), p. 395, and vol. iii. p. 347.

|| *Cours de Chymie* (1675), 2nd English edition (1686), p. 107.

According to his still more famous pupil Stahl, the litharge produced by the prolonged calcination of lead in air, is lead deprived of its phlogiston; but he and his followers were indifferent to the fact that when lead is burnt the weight of the resulting mass is greater than that of the original metal, and were content to insist that the burnt lead had lost its inflammable principle—that is, Phlogiston.

Tillet, assayer of the Paris Mint, made some quantitative experiments which led up in a singular way to the work of Lavoisier, who, as is well known, overthrew the old phlogistic theory by showing that a chemical combination takes place, resulting in an augmentation of weight which represents the exact weight of the gaseous body added. At the same time it should be remembered that the phlogistic chemists made a great step in advance, as was admitted by J. R. Mayer* in his memoir on the mechanical theory of heat; and Odling, discussing the experiments on the oxidation of lead, has pointed out† that an error has arisen in consequence of the same word being used in a different sense at different periods of time; chemists, in fact, now substitute the words potential energy for phlogiston, or, as Dr. Crum Brown well observed,‡ we recognise “that no compound contains the substances from which it was produced, but that it contains them *minus* something. We know now what this something is, and can give it the more appropriate name of potential energy; but there can be no doubt that this is what the chemists of the seventeenth century meant when they spoke of phlogiston.”

It will thus be evident that the main aim of chemical investigation down to the end of the last century was the explanation of calcination, combustion, or oxidation, and that lead was especially useful in solving the problem. It might, perhaps, be added that the absorption of oxygen by molten litharge furnished Ste. Claire-Deville,§ a physicist and metallurgist, with an important step in the argument as to dissociation, thus connecting the history of the metal, lead, with the great advance on the borderland of chemistry and physics which has been made in modern times.

The above remarks will be sufficient to show that conclusions of the utmost importance in the history of chemical theory were based on the very ancient metallurgical process of cupellation of lead, a process which affords an appropriate illustration, because,

* *Bemerkungen über die Kräfte der unbelebten Natur*, Liebig's Ann., vol. xlii. (1842), p. 233.

† *Proc. Roy. Inst.*, vol. vi. (1871), p. 323.

‡ *Edin. Roy. Soc. Proc.*, vol. v. (1866), p. 328.

§ *Leçons sur la dissociation*, and Wurtz, *Dictionnaire de Chimie*, vol. I. (1868), p. 1174.

in the gradual development of the knowledge derived in the first instance from the metallurgy of lead, there is much that is typical of the mutual relation of theory and practice that still prevails.

Now, as in the past, in the study of metallurgy, a prominent position must be given to the production of high temperatures, as it will be obvious that metallurgists have principally to consider the reactions of the elements when under the influence of heat. In the first half of the present century, temperatures higher than the melting point of zinc had not been determined with any degree of certainty; but, in 1856, Henri St. Claire-Deville pointed out that chemistry at high temperature, that is to say, up to the blue-white heat at which platinum volatilises and silica fuses, remained to be studied, as under such conditions ordinary chemical reactions may be modified or even reversed. Subsequently, in conjunction with Troost, he gave certain fixed points, such, for instance, as the boiling-points of cadmium and zinc; and his researches on dissociation have entirely modified the views generally entertained in regard to the theory of combustion. Indeed, so much is due to this illustrious teacher, that the best homage that can be offered to his memory will be to work in the directions he has indicated.

Deville's experiments on dissociation have rendered it possible to extend to the groups of atoms in chemical systems the laws which govern the fusion and vaporisation of masses of matter, and this has produced a revolution comparable in its importance to that which followed the discovery of the law of definite proportions, for dissociation has shown us that true causes of chemical change are variations of pressure and of temperature. For instance, oxygen may be prepared on an industrial scale from air by the intervention of oxide of barium heated to a constant temperature of 700° , provided air be admitted to the heated oxide of barium, under a pressure of $1\frac{1}{2}$ atmospheres, while the oxygen, thus absorbed, is evolved if the containing vessel be rendered partially vacuous. It will be evident, therefore, that at a certain critical temperature and pressure the slightest variation of either will destroy the equilibrium of the system and induce chemical change.

It will be clear that the measurement of high temperatures has become a question of much moment, and in this direction remarkable progress has recently been made.

The essential difference in the properties of metals produced by a small quantity of foreign matter introduces one very distinctive feature of metallurgy—the enormous influence exerted on a large mass of metal by a “trace” of another metal or metalloid, that is, by a quantity so small that it appears to be

out of all proportion to the mass in which it is distributed ; and it may safely be asserted, that in no other branch of applied science has the operator to deal with quantities that are at once so vast and so minute.

It may be that the "trace" is alone of value, as, for instance, the few grains of gold that can be profitably extracted from a ton of material, which, though containing only one part of gold in five millions by volume, is thereby entitled to be regarded as an auriferous deposit that can be profitably worked ; or it may be that the presence of a minute percentage of a metalloid is prejudicial and must be extracted, in order that the physical properties of the remaining mass of metal may not be such as to render it useless. Due prominence is given to such facts in the following pages.

It is assumed throughout that the student possesses a certain amount of chemical knowledge, but it will be evident that Metallurgical Chemistry is a special branch of chemical science which does not come within the ordinary sphere of the academic teaching of chemistry. It is often urged that metallurgical practice depends upon the application of chemical principles which are well taught in every large centre of instruction in this country, but a long series of chemical reactions exist which are of vital importance to the metallurgist, though they are not set forth in any British manual of chemistry, nor are dealt with in courses of purely chemical lectures. It is well to insist upon this point, because purely analytical and laboratory methods are so often given in the belief that they are applicable to processes conducted on a large scale and at high temperatures.

It is urged that technical instruction should be kept apart from scientific education, which consists in preparing students to apply the results of past experience in dealing with entirely new sets of conditions, but it can be shown that there is a whole side of metallurgical teaching which is truly educational, and leads students to acquire the habit of scientific thought as surely as the investigation of any other branch of knowledge.

It is, in fact, hardly possible in a course of theoretical chemistry, to devote much attention to specific cases of industrial practice in which reactions are incomplete because they are limited by the presence of bodies that cannot be directly eliminated from the chemical system. Take, for instance, the long series of reactions, studied by Plattner, who published the results of his investigations in his celebrated treatise, "*Die Metallurgische Röstprozesse*," Freiberg, 1856. A complex sulphide, of which copper is the main metallic constituent,

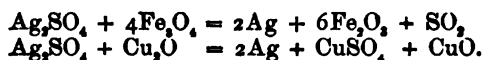
contains some fifty ounces of silver to the ton, and the problem may be supposed, for the present, to be limited to the extraction of the precious metal from the mass in which it is hidden. The student deriving his knowledge from an excellent modern chemical treatise would find the case thus stated:—

“Ziervogel's process depends upon the fact that when argentiferous copper pyrites is roasted, the copper and iron sulphides are converted into insoluble oxides, whilst the silver is converted into a soluble sulphate which is dissolved out by lixiviating the roasted ore with hot water, the silver being readily precipitated from this solution in the metallic state.”

It is certain that if an observant, chemically trained student visited a silver extraction works, and possessed sufficient analytical skill to enable him to secure evidence as to the changes that occur, he would find a set of facts which his training had not enabled him to predict, and he would establish the existence of a set of reactions to the nature of which his chemical reading had hardly given him a clue. The process to be considered is a simple one, but it is typical, and applies to a large proportion of the 7,000,000 ounces of silver annually obtained in the world from cupriferous compounds. He would be confronted with a ton or more of finely divided material spread in a thin layer over the bed of a reverberatory furnace. Suppose the material is what is known as a complex “regulus” as imported into Swansea or produced at Frieberg, to which are added rich native sulphides. The mixture then consists of sulphides mainly of iron and copper, with some sulphide of lead, and contains fifty or sixty ounces of silver to the ton, and a few grains of gold. It may also contain small quantities of arsenic and antimony as arsenides, antimonides, and sulpho-salts, usually with copper as a base.

The temperature of the furnace in which the operation is to be performed is gradually raised, the atmosphere being an oxidising one. The first effect of the elevation of the temperature is to distil off sulphur, reducing the sulphides to a lower stage of sulphurisation. This sulphur burns in the furnace atmosphere to sulphurous anhydride (SO_2), and coming in contact with the material undergoing oxidation is converted into sulphuric anhydride (SO_3). It should be noted that the material of the brickwork does not intervene in the reactions, except by its presence as a hot porous mass, but its influence is, nevertheless, considerable. The roasting of these sulphides presents a good case for the study of chemical equilibrium. As soon as the sulphurous anhydride reaches a certain tension the oxidation of the sulphide is arrested, even though an excess of oxygen be

present, and the oxidation is not resumed until the action of the draught changes the conditions of the atmosphere of the furnace, when the lower sulphides remaining are slowly oxidised, the copper sulphide being converted into copper sulphate mainly by the intervention of the sulphuric anhydride formed as indicated. Probably by far the greater part of the iron sulphide only becomes sulphate for a very brief period, being decomposed into the oxides of iron, mainly ferric oxide, the sulphur passing off. Any silver sulphide that is present would have been converted into metallic silver at the outset were it not for the simultaneous presence of other sulphides, notably those of copper and of iron, which enables the silver sulphide to become converted into sulphate. The lead sulphide is also converted into sulphate at this low temperature. The heat is now raised still further with a view to split up the sulphate of copper, the decomposition of which leaves oxide of copper. If, as in this case, the bases are weak, the sulphuric anhydride escapes mainly as such; but when the sulphates of stronger bases are decomposed the sulphuric anhydride is to a great extent decomposed into a mixture of sulphurous anhydride and oxygen. The sulphuric anhydride, resulting from the decomposition of this copper sulphate, converts the silver into sulphate, and maintains it as such, just as, in turn, at a lower temperature, the copper itself had been maintained in the form of sulphate by the sulphuric anhydride eliminated from the iron sulphate. When only a little of the copper sulphate remains undecomposed, the silver sulphate begins to split up, and the furnace charge must therefore be immediately withdrawn, or the whole of the silver sulphate would be converted into metallic silver, partly by the direct action of heat alone, and partly by reactions such as those shown in the following equations:—



If the charge were not withdrawn, the silver would thus be effectually removed from the solvent action of water, and the smelter's efforts would have failed entirely. The charge still contains lead sulphate, which cannot be completely decomposed at any temperature attainable in the roasting furnace, except in the presence of silica, and it is well to leave it where it is if the residue has subsequently to be smelted with a view to the extraction of the gold. The elimination of arsenic and antimony gives rise to problems of much interest, and again confronts the smelter with a case of chemical equilibrium. For the sake of

brevity it will be well for the present to limit the consideration to the removal of antimony, which may be supposed to be present as sulphide. Some sulphide of antimony is distilled off, but this is not its only mode of escape. An attempt to remove antimony by rapid oxidation would be attended with the danger of converting it into insoluble antimonates of the metals present in the charge. In the early stages of the roasting it is therefore necessary to employ a very low temperature, and the presence of steam is found to be useful as a source of hydrogen, which removes sulphur as hydrogen sulphide, the gas being freely evolved. The reaction $\text{Sb}_2\text{S}_3 + 3\text{H}_2 = 3\text{H}_2\text{S} + 2\text{Sb}$ between hydrogen and sulphide of antimony is, however, endothermic, and could not, therefore, take place without the aid which is afforded by external heat. The facts appear to be as follows: sulphide of antimony, when heated, dissociates, and the tension of the sulphur vapour would produce a state of equilibrium if the sulphur thus liberated were not seized by the hydrogen and removed from the system. The equilibrium is thus destroyed and fresh sulphide is dissociated. The general result being that the equilibrium of the system is alternately restored and destroyed until the sulphide is all decomposed. The antimony combines with oxygen and escapes as volatile oxide, as does also the arsenic, a portion of which is volatilised as sulphide.

The main object of the process which has been considered, is the formation of soluble sulphate of silver. If arsenic and antimony have not been eliminated, their presence at the end of the operation will be specially inconvenient, as they give rise to the formation of arseniate and antimoniate of silver, insoluble in water, which may necessitate the treatment of the residues by an entirely different process from that which has hitherto been considered.

It will have been evident that effecting this series of changes demands the exercise of the utmost skill, care, and patience. The operations beginning at a dull red heat, or a temperature of some 500° , are completed at 700° , within a range, that is, of 200° . Judicious stirring has been necessary to prevent the formation of crusts of sulphates, which would impede the reactions, and, as has been shown, an undue elevation of temperature within a very limited range would, at any stage, have been fatal to the success of the operation. It is difficult to appreciate too highly the delicacy of sight and touch which enables an operator to judge by the aid of rough tests, but mainly from the tint of the streak revealed when the mass is rabbled, whether any particular stage has or has not been reached, and it will be obvious that the

requisite skill is acquired solely by observation and experiment. The technical instructor may impart information as to the routine to be followed, and the appearances to be observed, but scientific knowledge of a high order can alone enable the operator to contend with the disturbing influences introduced by the presence of unexpected elements or by untoward variations in temperature. In the training of a metallurgist it is impossible to separate education from instruction, and the above description of a very ordinary operation will show the intimate relations between science and practice which are characteristic of metallurgical operations. Practice is dependent on science for its advancement, but scientific workers too often hesitate to attack metallurgical problems, and to devote the resources of modern investigation to their solution, because they are not aware of the great interest of the physical and chemical problems which are connected with many very simple metallurgical processes, especially with those that are conducted at high temperatures.

Proceeding yet one step further, suppose that the copper smelter takes possession of the residual mass, consisting mainly of oxide of copper, he would smelt it with fresh sulphide ores and obtain, as a slag from the earthy matters of the ore, a ferrous silicate containing some small proportion of copper. The displacement of the copper from this silicate may be effected by fusing it with sulphide of iron, a fusible sulphide of iron and copper being formed which readily separates from the slag. By this reaction some twenty thousand tons of copper are added to the world's annual production. Proceeding a step further, suppose the smelter to have reduced his copper to the metallic state. If arsenic had been originally present in the ore, and had not been eliminated entirely in the roasting, extraordinary difficulties would be met with in the later stages of the process, in extracting small quantities of arsenic which resist the smelter's efforts. Copper, moreover, containing above one per cent. of arsenic cannot be 'overpoled,' as the presence of arsenic hinders the action of gases on the copper. The amount of arsenic which the copper smelter has to remove may vary from mere traces up to one per cent., and if the copper is destined for the use of the electrical engineer, he will insist on its being as pure as possible, for the presence of a trace of arsenic would materially increase the electrical resistance of the copper, and would be fatal to its use in submarine telegraphy. If, on the other hand, the copper is intended for the maker of locomotive fire-boxes, he will encourage the retention of small quantities of arsenic, as it is found to actually increase the endurance of the copper, and the

smelter will in such a case have no inducement to employ a basic furnace lining, nor will he care to use the special methods for the removal of arsenic with which he is familiar. It may all seem simple enough, but the modern process of copper smelting has been laboriously built up, and has a long and interesting pedigree which may be traced to at least the eighth century, when Geber described the regulus 'coarse metal' as being 'black mixed with livid,' and our familiar 'blue metal' as being 'of a most clean and pleasant colour,' and indicated the reason for the difference.

It must not be supposed even when commercially pure copper lies on the furnace bed, ready to be transferred to moulds, that its turbulent career of reactions is over. It might be thought that the few tenths per cent. of impurity, dissolved oxide, and occluded gas, are so far attenuated by distribution that their interactions must be insignificant. This is far from being the case. The bath of metal is seething from its reactions until the copper is solid, and then polymerization begins. There may not be a sharply defined critical range of temperature within which the metal can alone be successfully worked, which varies, as regards its starting point, with the kind of impurity present, as is the case with steel; but evidence of molecular change in the solid metal is afforded by the pyrometric curves of cooling to which subsequent reference will be made in this work, and by the singular behaviour, as regards electrical resistance, of various samples of copper, in which chemical analysis hardly reveals a difference.

The above description of a very ordinary set of operations will serve to indicate the general nature of the problems with which the metallurgist has to deal.

CHAPTER II.

PHYSICAL PROPERTIES OF METALS.

Molecular Structure.—The physical aspects of metals are so pronounced as to render it difficult to abandon the old view that metals are sharply defined from other elements, and form a class by themselves. The term metal is in fact somewhat arbitrary. Zinc and bismuth, when they were first discovered, were considered to be semi-metals, and it was not until mercury was frozen by Braune in 1759 that it was recognised as a metal. Like all other elements, metals are composed of atoms grouped in molecules, and any force that alters the relations of the atoms in the molecules modifies the physical properties of the metals. Indeed, it would be easy to show that the physical constants of each metal vary with its degree of purity. The molecular grouping of metals is doubtless very varied, and little definite is known regarding the structural stability of most of them; but it may be assumed that it is not very great, as some metals split up into single atoms when they are volatilised, and most of them unite readily with chlorine and with oxygen.* It is probable that in many pure metals, such as gold, silver, copper and iron, the individual molecules are of simple atomic constitution, and that these fundamental molecules bear a uniform relationship to one another. Consequently, any mass, of which the fundamental molecules are the constituent particles, may practically be regarded as a single molecule. Two fundamental molecules must, however, be held to be capable of uniting to form complexes that have less power of cohering, and any circumstance tending to bring about the formation of such complexes would also tend to make the material less tough. This may account for the extraordinary alteration in the properties of many metals produced by very small quantities of incompatible foreign matters.† It will be shown in a future chapter that the effect produced by a small quantity of an im-

* Lothar Meyer, *Modern Theories of Chemistry*, English translation, 1888, p. 568.

† H. E. Armstrong, *Min. Proc. Inst. C.E.*, vol. xciii. (1888), p. 112.

purity added to a mass of metal bears a close relation to the atomic volume of the added element.

Density.—The density of a metal is dependent on the intimacy of the contact between the molecules. It is dependent, therefore, on the crystalline structure, and is influenced by the temperature of casting, by the rate of cooling, by the mechanical treatment, and by the purity of the metal. With the exception of bismuth, all metals are lighter when molten than when in the solid state. In the case of cast iron, which passes through a pasty state on solidification, the density is less in that state than in the fluid or solid. The density of a metal is augmented by wire-drawing, hammering, and any other physical method of treatment in which a compressing stress is employed. Mere traction, however, may diminish the density by tending to develop cavities in the metal. Pressure on all sides of a piece of metal increases its density. The density of standard gold, for example, by compression between dies is increased by 0.9, and cast discs of platinum, having a density of 21.21, may have the density increased to 21.46 by striking; whilst annealing such struck discs will again diminish their density. This shows that the compression is not permanent, and is solely due to the closing of pores. W. Spring* has even shown by careful experiments on lead, tin, bismuth, antimony, cadmium, aluminium, and zinc, that a pressure of 20,000 atmospheres continued for many days is insufficient to effect the obliteration of all the pores. A metal can only be really compressed if the result of the application of pressure is to cause it to pass to an allotropic state, that is denser than that which it originally possessed. The specific gravities of the various metals are given in the table on p. 58. Lithium is the lightest metal, and iridium the heaviest, the specific gravity of the former being 0.6, and that of the latter 22.38.

So early as 1845, Joule† recognised the importance of determining the specific gravity of melted metals, seeing that "this condition would completely obviate the influence of cohesion, or that of any particular molecular arrangement." His method, which was essentially that afterwards adopted by Mallet‡ and by the author,§ may be described as follows:—It consists in filling with molten metal a vessel, the capacity of which may be calculated for the particular temperature at which the molten metal is introduced. The weight of the metal when cold, divided by the

* *Bull. Soc. Chim. Paris*, vol. xxxix. (1883), p. 515; and Gray, *Proc. Roy. Soc.*, vol. liv. (1893), p. 283.

† *Collected Papers*. Published by the Physical Society, vol. ii. p. 136.

‡ *Proc. Roy. Soc.*, vol. xxii. (1873), p. 366; and vol. xxiii. (1874), p. 209.

§ *Ibid.*, vol. xxiii. (1875), p. 481.

weight of water which the expanded vessel is capable of holding, gives the fluid density of the molten metal. Subsequently, working in conjunction with T. Wrightson, the author* determined, by the aid of an instrument called the oncosimeter, devised by the former, the fluid density of several metals. The results which have as yet been obtained may be briefly summarised in the following table:—

—	Specific Gravity of Solid.	Fluid Density.		Percentage of Change in Volume from Cold Solid to Liquid.
		By Mallet's Method.	By Oncosimeter.	
Bismuth . . .	9.82	10.039	10.055	Decrease of vol. 2.30
Copper . . .	8.80	—	8.217	Increase of vol. 7.10
Lead . . .	11.40	10.650	10.370	" " 9.93
Tin . . .	7.50	6.974	7.025	" " 6.76
Zinc . . .	7.20	6.550	6.480	" " 11.10
Silver . . .	10.57	9.460	9.510	" " 11.20
Iron (No. 4 foundry pig) . .	6.95	—	6.880	" " 1.02
Iron, cast (mixed brands) . . .	7.17	6.650		

The question of the fluid densities has also been investigated by Nies and Winkelmann,† who have adopted another method, determining the liquid density by observing the weights of blocks which just sink and just swim. With regard to bismuth, C. Lüdeking‡ finds that this metal, like water, attains a maximum density just before becoming solid, the expansion at the moment of solidification being about 3 per cent. of the volume.

Fracture.—The appearance of the fractured surface of a metal depends partly on the nature of the metal and partly on the manner in which solidification occurred. Sudden cooling to a great extent prevents the formation of crystals, whilst slow cooling facilitates their development. Long-continued hammering, frequent vibrations, and intense cold will produce the latter result. Any condition that affects either the cohesion or the crystalline structure of a metal affects its fracture. Thus, lead broken when hot has a columnar structure; when broken cold, this structure is not exhibited.

* *Phil. Mag.*, vol. xi. (1881), p. 295; vol. xiii. (1882), p. 360.

† *Sitzungsber. der Acad. der Wissen. zu München*, 1881, p. 63.

‡ *Ann. Phys. Chem.*, vol. xxxiv. (1888), p. 21.

The ordinary mineralogical terms regarding colour and fracture are used in relation to metals. Practice, however, can alone enable the student to accurately describe these appearances.

Malleability.—This is the property of permanently extending in all directions, without rupture, by pressure produced by slow stress or by impact. As a rule, crystalline metals are not malleable, and any circumstance that tends to produce crystallisation must affect the malleability. Thus, in nearly all metals the malleability becomes impaired when they are subjected to rolling or long-continued hammering; but this property may be regained by annealing, which consists in raising the metal to a high temperature and allowing it to cool, either rapidly or slowly, usually the latter. At different temperatures metals behave in different ways; some are malleable when at a red heat, but not so when cold. These are defined as being *cold-short*. Others are malleable when cold, but not when at a red heat. These are described as being *red-short*. Some metals are malleable at all temperatures, others are not malleable at all. Zinc is brittle when cold and when hot, but at a temperature of 150° it is malleable. The malleability of a metal is dependent on its purity. Relative malleability may be determined by the degree of thinness of the sheets that can be produced by beating or rolling the metals, without annealing.

Ductility is the property that enables metals to be drawn into wire. It generally decreases with an increase in the temperature of the wire at the time of drawing, but there is no regular ratio between the two. Iron is less ductile at 100° , and more ductile at 200° , than it is at 0° . Malleable metals are also ductile, but they do not possess the two properties in the same order. Arranged according to their malleability, the more important metals follow this order:—1. Gold; 2. Silver; 3. Copper; 4. Tin; 5. Platinum; 6. Lead; 7. Zinc; 8. Iron; 9. Nickel. The order of ductility, on the other hand, is:—1. Gold; 2. Silver; 3. Platinum; 4. Iron; 5. Nickel; 6. Copper; 7. Zinc; 8. Tin; 9. Lead. The rate at which the traction is applied, exercises an important influence on the properties of malleability and ductility.

Tenacity is the property possessed by metals, in varying degrees, of resisting the separation of their molecules by the action of a tensile stress.

Toughness is the property of resisting the separation of the molecules after the limit of elasticity has been passed.

Hardness is the resistance offered by the molecules of a substance to their separation by the penetrating action of another sub-

stance. Great differences are observable between the hardness of the different metals. The results of the experiments of Bottone gave valuable information. In his scale the hardness of the diamond was found to be 3010, whilst the relative hardness of twenty metals was determined with the following results :—

Manganese	1456	Gold	979
Cobalt	1450	Aluminium	821
Nickel	1410	Cadmium	760
Iron	1375	Magnesium	726
Copper	1360	Tin	651
Palladium	1200	Lead	570
Platinum	1107	Thallium	565
Zinc	1077	Calcium	405
Silver	990	Sodium	400
Iridium	984	Potassium	230

In these determinations the time necessary to produce a cut of definite depth was taken as a measure of the hardness of the material, and Bottone concluded that the hardness so obtained was proportional to the specific gravity of the metal divided by its atomic weight. Metals that possess high limits of elasticity are usually very hard. The softness increases with an increase of temperature. Mr. T. Turner,* of the Mason College, Birmingham, a former pupil of the author, has also investigated the hardness of metals and devised a useful instrument for the purpose.

Brittleness is the sudden interruption of molecular cohesion when the substance is subjected to the action of some extraneous force, such as a blow or a change of temperature. It is largely influenced by the purity of the metal.

Elasticity, Extensibility, and Strength of Metals.—At first sight it might seem that testing the mechanical properties of metals is more within the province of the engineer than that of the metallurgist. The latter has, however, not only to extract metals from their ores, but also to fit them for use. He must therefore know what mechanical properties† are possessed by the more important metals and alloys, and be able to submit them to experimental tests instead of merely trusting to statements recorded by others.

Elasticity is the power a body possesses of resuming its original form after the removal of an external force which has produced a change in that form. The point at which the elasticity and

* *Proc. Birmingham Phil. Soc.*, vol. v. part 2.

† The more important recent works dealing with this subject are:—Kennedy, *Proc. Inst. C.E.*, vol. lxxxviii. (1887), p. 1; Unwin, *Testing of Materials of Construction*, 1888; Lebasteur, *Les Métaux à l'Exposition Universelle*, 1878. J. Régal, *Constructions Métalliques: Élasticité et résistance des matériaux*, 1892.

the applied stress exactly counterbalance each other, is termed the limit of elasticity. If the applied stress were then removed, the material acted upon would resume its original form. If, however, the stress were increased, the change in form would become permanent, and permanent set would be effected. Within the limit of elasticity, a uniform rod of metal lengthens or shortens equally under equal additions of stress. If this were the case beyond that limit, it is obvious that there would be some stress that would stretch the bar to twice its original length, or shorten it to zero. This stress, expressed in lbs. or tons for a bar of 1 inch square cross section is termed the modulus of elasticity. As an illustration, let it be supposed that a bar of steel 1 inch square is stretched to its limit of elasticity by a force of 139,000 lbs., and to have elongated under the action of this stress 0.00418 inch, the modulus of elasticity of this bar would be the force that would be required to elongate it by 1 inch, and this would be—

$$0.00418 : 1.0 :: 139,000 : x$$

$x = 33,253,588$ lbs. per square inch. Hence the modulus of elasticity is a stress that bears the same proportion to the original length of a uniform bar as the stress that will produce any given amount of strain bears to the length of this strain, the term stress meaning an equilibrating application of force to a body, and the term strain meaning any definite alteration of form or dimensions sustained by that body. The modulus of elasticity may thus be defined as being the number obtained by dividing the number expressing the stress by that expressing the strain that it produced. Unwin expresses this as follows:—

Let p be the stress reckoned on unit of area, and λ the extension or compression reckoned per unit of length.

Then, by Hooke's law— $\frac{p}{\lambda} = E$, a constant which is termed the coefficient of direct elasticity, or Young's modulus. It has the same value for tension and compression.

Thus, to take the above case of a hardened sample of steel in which the extension up to the limit of elasticity was small, the load, however, being considerable:—

Load up to limit of elasticity, 139,000 lbs. per square inch.

Extension up to limit of elasticity, 0.00418 inch.

$$E = \frac{139,000}{0.00418} = 33,250,000 \text{ lbs. per square inch.}$$

Professor Kennedy finds the specific extension to be a quantity most useful in works. This is the extension in thousandths of an inch on a length of 10 inches under a stress of 1000 lbs.

per square inch. Its reciprocal, multiplied by 10 millions, is the modulus of elasticity in lbs. per square inch.

In measuring the strength of metals, it is necessary to determine—

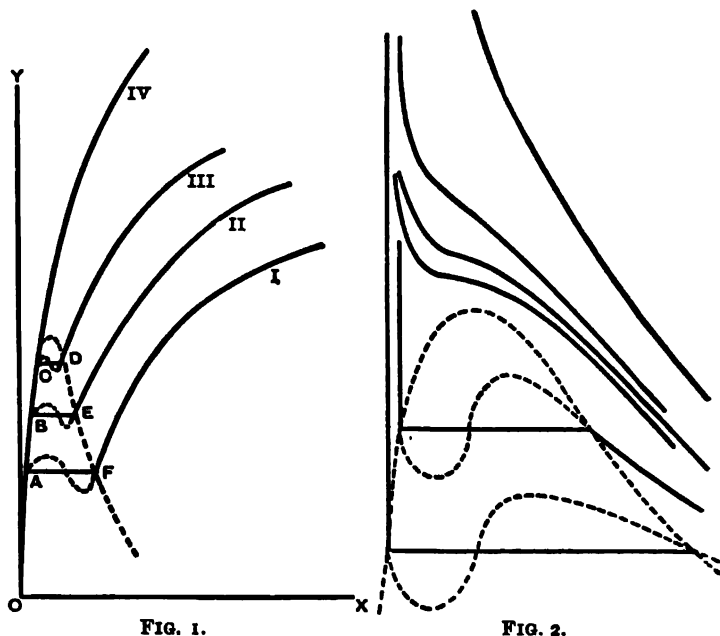
1. The greatest stress the metal can sustain within the limit of elasticity ;
2. The strain within the limit of elasticity ;
3. The total extent of the strain, or alteration of form before rupture takes place ;
4. The ultimate tensile strength or maximum stress the material can sustain without rupture.

The limit of elasticity and the breaking stress are the points which have usually to be determined, and these alone will be considered here. For information as to torsional and compression tests, the student is referred to the works of Unwin and Kennedy.

In testing a piece of metal, the first point to be determined is the limit of elasticity. When a metal, such as iron or steel, is submitted to stress by pulling its ends in opposite directions, it stretches uniformly throughout its length. There is, however, in such a solid a limit in the application of the stress up to which the metal, if released, will return to its normal length. This point is the limit of elasticity. It is, however, certain that a very small application of load produces permanent deformation, so that the determination of the exact limit of elasticity will depend upon the delicacy of the instruments used for its measurement. It is safe to consider the limit of elasticity to be the point at which the stresses and strains cease to be exactly proportional. If the strains are plotted as abscissæ and the stresses as ordinates, points will be obtained on a curve giving the relation of stress and strain for the whole test. Up to the limit of elasticity, this curve is almost a straight line ; but when that point has been reached, the molecular arrangement of the metal breaks down, and, as Professor Unwin expresses it, probably the breaking down point (which is not to be confounded with the limit of elasticity*), is a kind of physical record of the condition of constraint in the bar at the moment of rolling or hammering. It has been shown by Osmond that in the case of iron or steel, any stress which produces a permanent deformation is attended by a re-arrangement of the atoms within the molecules of the metal. This will be shown in a subsequent chapter to mark the passage of iron into an allotropic state. In support of this view, it may be mentioned

* See also Gautier, "Discussion on Testing Machine," *Journ. Iron and Steel Inst.*, vol. ii. (1888), p. 31.

that Carus Wilson,* has examined this point of the stress-strain curve with much care; and shows that the peculiar bending of the curve indicates the condition of strain in a steel bar, since by gradually increased stress the steel may be converted from an elastic solid to a viscous fluid. He compares such curves (I to IV) for steel of different hardness with the stress-strain curves of a gas at different temperatures, there being strong probability that in both cases the apparent discontinuity, at AF, BE, and CD, is really a double inflection due to a change taking place piecemeal through-



out the mass. Figs. 1 and 2 show Carus Wilson's curve for the yield-point of steel, and Andrew's curve exhibiting the passage of carbonic anhydride from the gaseous to the liquid state. Probably the increase in the breaking stress and diminution in the elongation, which has been found to result from the application of long continued stress to steel, is the result of the molecular change in the metal. It is also known that the prolonged application of a

* *Phil. Mag.*, vol. xxix. (1890), p. 200

load to steel raises the elastic strength. This appears to afford additional evidence of molecular change. If the load is slowly applied the stress-strain curve will be flatter than if it is applied rapidly. Colonel Maitland* has conclusively shown that in the case of unhardened steel used for the manufacture of guns, the ultimate elongation is increased from 27 to 62 per cent. by rapid application of the load.

It is important to ascertain in what way the mechanical properties of metals are modified when they are submitted to tests while hot. André le Chatelier† has published some experiments in this direction in connection with a research on the influence of temperature on the mechanical properties of iron and steel. His results as regards a pure variety of "cinder free" ingot iron containing 0.05 per cent. of carbon, and steel with 0.8 per cent. of carbon are given in the curves (Fig. 3). The amount of man-

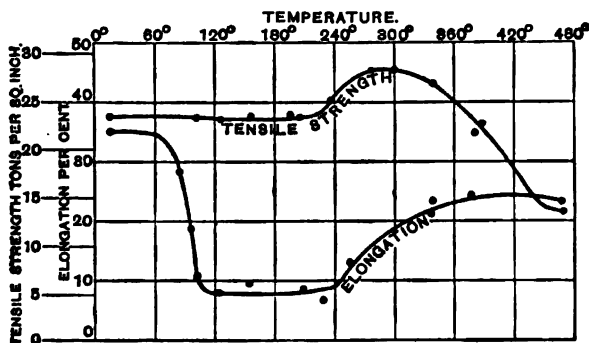


FIG. 3.

ganese varied from 0.35 per cent. to 0.4 per cent. The effect of heat is to produce two modifications in the mechanical properties of iron and steel; one of these becomes evident at 80°, the second at about 240°. These changes depend both on the temperature and on the speed with which the load is applied. The fragility of iron to shock is at its maximum at 300°, but it also possesses at this temperature a maximum resistance both to longitudinal stress and to extension if the load is slowly applied.

With reference to the strength of alloys at different temperatures,

* *Min. Proc. Inst. C.E.*, vol. lxxxix, p. 120.

† *Comptes Rendus*, vol. cix. (1889), p. 58. For effect of cold, see Dewar, note on p. 57.

Prof. Unwin* observes that, in the case of commonly used alloys, such as gun-metal and brass, the question is one of practical importance. Some experiments made by him in 1877 for the Admiralty proved that Muntz-metal and phosphor-bronze showed a fairly regular decrease in tenacity as the temperature was raised to 260° , but in the case of gun-metal the tenacity diminished regularly up to a temperature of 150° to 175° , while beyond that temperature there was a sudden decrease of tenacity, generally of more than 50 per cent., and in several cases at a temperature of 260° the tenacity had become *nil*. This is important, because at the high pressures and correspondingly high temperatures at which steam-engines are often worked, gun-metal may be exposed to temperatures of 175° to 230° , and in order to ascertain whether at such temperatures the strength of such alloys is seriously impaired, Prof. Unwin has made a further series of experiments. The results showed that with yellow-brass, Muntz-metal, and Delta-metal the decrease of tenacity follows a regular law without any sudden loss of strength. Even at temperatures of 315° to 345° , all the bars had a not inconsiderable tenacity. The ultimate elongation of the bars was measured, and a peculiarity in the influence of temperature was observed. In most cases the ultimate elongation diminishes with increase of temperature. With Muntz-metal the decrease is regular, and there is still a considerable elongation before fracture at temperatures above 340° . With yellow-brass the decrease is more rapid, and there is very little elongation before fracture at temperatures above 260° . The elongations of the gun-metal bars were very irregular, and at temperatures of over 260° the elongations were but small. On the other hand, in the case of Delta-metal bars, the elongation increased regularly with the increase of temperature. The composition of the above-named alloys will be found in Chap. III.

The following series of curves (Fig. 3a) shows the results obtained with copper of varying degrees of purity at temperatures ranging between 15° C. and 470° . It will be observed that the effect of bismuth is very noteworthy.†

The elasticity and strength of metals are determined by the aid of testing machines, the more important of which are based on Kirkaldy's constructive principle of applying the load by water pressure and measuring it by dead weight. In small machines, the hydraulic ram may be replaced by a screw and gearing. Figs. 4 to 7, copied from Prof. Kennedy's admirable paper on engineering

* Report. Brit. Assoc. 1889, p. 746.

† Inst. Mech. Eng. Proc. 1893 p. 102.

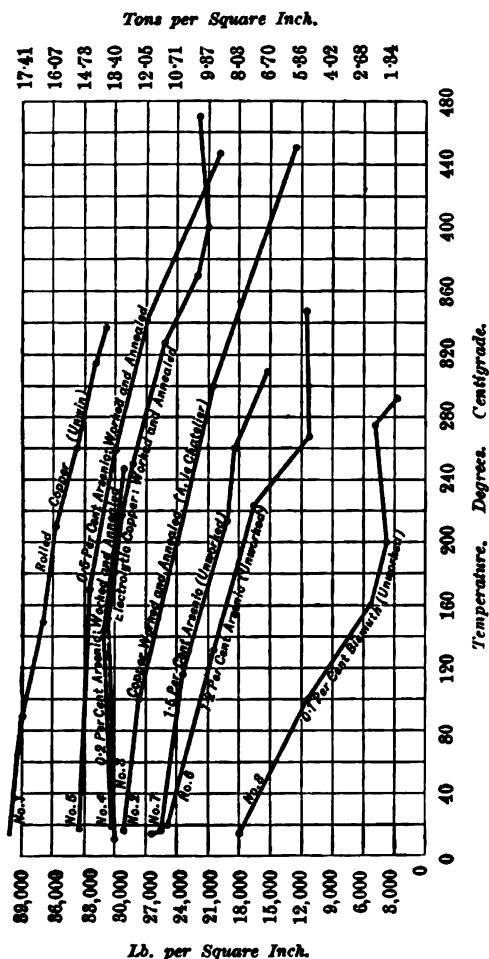


FIG. 3a.—TENSILE STRENGTH OF COPPER RODS.

laboratories,* illustrate the principle of several types of testing machine, without indicating their proportions. The Werder machine (Fig. 4) is largely used on the Continent. The test piece, *a*, is held at one end in the frame of the machine, *e*, and at the other pulled from the short arm, *c*, of a knee lever, to the long arm of

* *Min. Proc. Inst. C.E.*, vol. lxxxviii. (1887), p. 1.

which hangs a scale-pan, d . The ratio of c_2 to c_1 is 500 : 10. The central fulcrum of the lever rests on the end of the ram, b , so that the whole measuring apparatus moves along as the piece extends

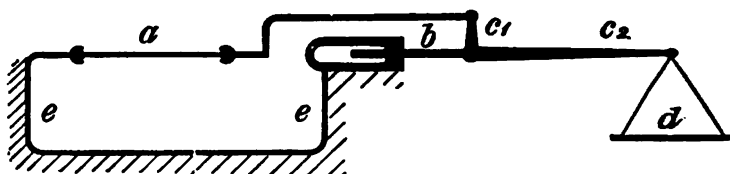


FIG. 4.

and the ram moves out, the arm, c_2 , being always kept horizontal by the aid of a spirit level.

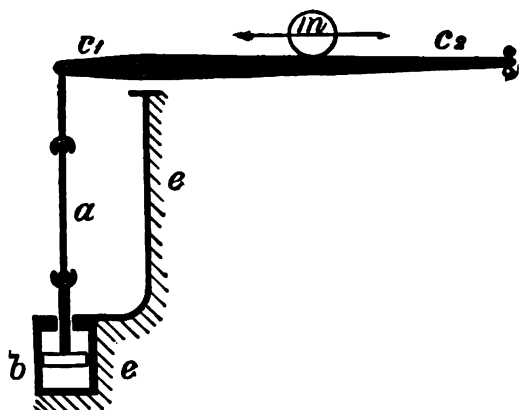


FIG. 5.

Wicksteed's machine* (Fig. 5) is a vertical one with a single lever, $c_1 c_2$, placed horizontally on the top. A movable poise, m , measures the load, pressure being applied to the ram, b , by a screw or pump. The ratio of c_2 to c_1 is 50 : 1. In a 100-ton machine, the weight, m , is 1 ton, so that it balances a pull of 50 tons when at the end of c_2 . To carry the load on to 100 tons, m is run back beyond the fulcrum, and a second weight of 1 ton is hung to the end of c_1 . The poise weighs 1 ton, and is moved along the lever by a screw worked by power. Each 3 inches of movement of the poise adds 1 ton to the load on the test-piece, whilst a vernier

* *Inst. Mech. Eng. Proc.*, 1882, p. 384.

attached to the poise may be read, on a scale affixed to the lever, to one-hundredth of a ton.

Greenwood's machine (Fig. 6) is in use in the laboratory of Professor Kennedy, by whom the original type has been con-

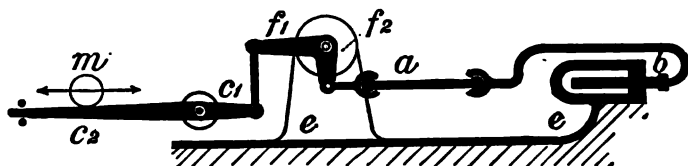


FIG. 6.

siderably improved. It is a horizontal machine with two levers, a knee lever, f_2, f_1 ($5 : 1$), and a steel-yard, c, c_1 ($20 : 1$), the total leverage being $100 : 1$. The load is applied by the ram, b , and measured by the position of the poise, m , on the steel-yard.

Gollner's machine (Fig. 7) is a double-lever vertical machine,

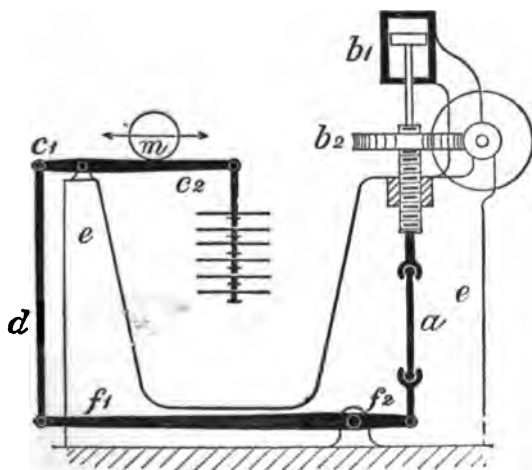


FIG. 7.

working up to 20 tons. Both screw and ram may be provided, with means for changing at once from one to the other. For light tests, the lever, f_1, f_2 , can be disconnected, and the machine used as a single lever machine. This type of testing machine is that used in the laboratory of the Royal School of Mines, and a

rough perspective sketch of it, in the opposite position to Fig. 7, is given in Fig. 8.

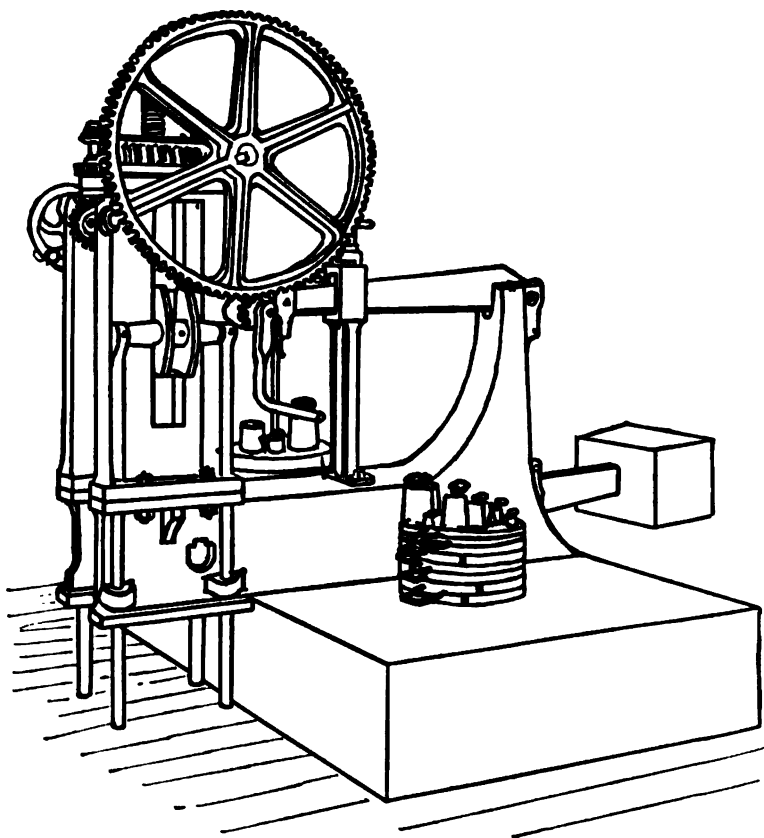


FIG. 8.

In a testing machine it is extremely desirable to have some apparatus by the aid of which the stress-strain diagram of a piece of metal under test may be drawn automatically. The most successful apparatus of this kind is that devised by Wicksteed*

* *Inst. Mech. Eng. Proc.*, 1886, p. 27. For descriptions of American machines consult *Testing Machines: their History, Construction and Use*, by A. V. Abbott. New York, 1884.

(Fig. 9). In this, the motion of the pencil that indicates the load is derived from the pressure in the hydraulic press, and not from the weighing apparatus, a wire attached by clips to the specimen serving to rotate a recording drum by an amount proportional to the elongation. The pencil having an axial motion proportional

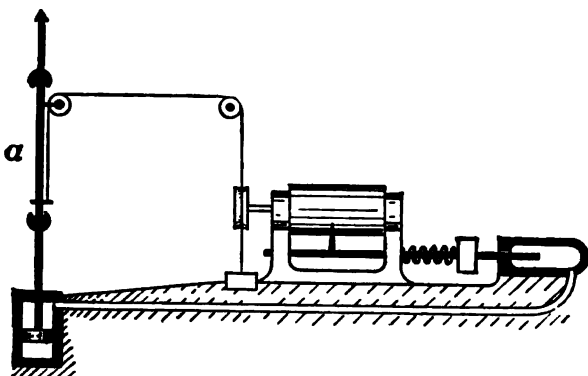


FIG. 9.

to the load, and the drum a rotating motion proportional to the extension, a stress-strain diagram is described.

The following table gives the ultimate tensile strength of a number of metals in lbs. avoirdupois per square inch:—

Copper, cast . . .	19,000	Steel, low-carbon . . .	90,000
" sheet . . .	30,000	" high-carbon . . .	132,000
" bolts . . .	36,000	Lead, sheet . . .	3,300
" wire . . .	60,000	Tin, cast . . .	4,600
Iron, cast, weak . . .	13,400	Zinc . . .	7,000
" average . . .	16,500		18,000
" strong . . .	29,000	Gold, pure, cast . . .	15,680
Iron, wrought, plates . . .	51,000	Aluminium, castings . . .	15,000
" bars & bolts . . .	60,000	" sheet . . .	24,000
" hoop . . .	64,000	" wire . . .	30,000
" wire . . .	90,000	" bars . . .	28,000

Influence of Foreign Elements on the Strength of Metals.—The influence of chemical composition on the mechanical properties of metallic masses is of great importance; this has long been recognised, but it is singular that the subject has been so little investigated. Turn, for instance, to Dr. Percy's classical work on Iron and Steel, published in 1864. It fully represents the information which had been gained at that time, yet it con-

tains the results of but few mechanical tests on the materials with which it deals.

The influence of foreign elements are best shown in the case of iron. The properties of this metal are absolutely changed by the presence of a few tenths per cent. of carbon; but it may be doubted whether the exact influence exerted by varying proportions of carbon has been accurately determined. A distinguished authority, Mr. H. M. Howe, thinks that it is not yet known, for, in an elaborate work recently published on the *Metallurgy of Steel* (New York, 1890), which will be of much service to the student, he points out that he has plotted, in a single curve, the results of over 2500 tests, and yet the conclusion he arrives at is, that we are not at present able to quantitatively express the effect of carbon. The fact is, that metallurgists are only beginning to realise that the effect of elements in the presence of each other is very complicated, and that it is absolutely necessary to study the effect of any given element on an absolutely pure mass of the metal to be tested. With regard to iron, the author has shown* that the tensile strength of electro-deposited iron, which is as pure as any iron can be, is 2.7 tons per square inch before annealing, and 15.5 tons per square inch after annealing. Even in this case, however, it is doubtful how far the result is influenced by the presence of occluded hydrogen, or by the fact that electrolytic iron is probably an allotropic form of the metal. In studying the effect of carbon, it is very difficult, therefore, to start from pure iron as an absolute basis. It may be sufficient, however, for the student to keep steadily in mind the very useful diagram, represented in Fig. 10, by which Deshayes† has indicated the effect of carbon, and incidentally that of manganese, on the tensile strength of iron. The co-ordinates are respectively percentages of carbon and tensile strengths expressed in tons per square inch. The effect of carbon is indicated by the dark continuous line, and that of varying proportions of manganese in the presence of carbon by the thin continuous, and the dotted lines. The effect of a given proportion of carbon is found by producing a vertical line, from the point indicating the percentage of carbon, until it cuts the darker curve, so that the tensile strength will be represented by the length of this vertical line. It may be added that, according to some authorities, the maximum strength would be attained in steel containing 0.8 to 1.0 per cent. of carbon, after which point the line representing tensile

* *Journ. Iron and Steel Inst.*, No. 1. (1887), p. 74.

† *Classement et emploi des Aciers* (Paris, 1880), p. 151.

strength falls rapidly. This is also shown by the dotted curve in Fig. 14, p. 35.

The tenacity of carburised iron is, however, greatly affected by the "mode of existence" of carbon in the iron, as will be shown in Chapter IV., which deals with the thermal treatment of metals. It will therefore be evident that it is only possible for any curve to represent in a very general way the influence of carbon on iron, and this is specially true of the highly carburised varieties of iron known as cast iron.

INFLUENCE OF CARBON & MANGANESE ON IRON.

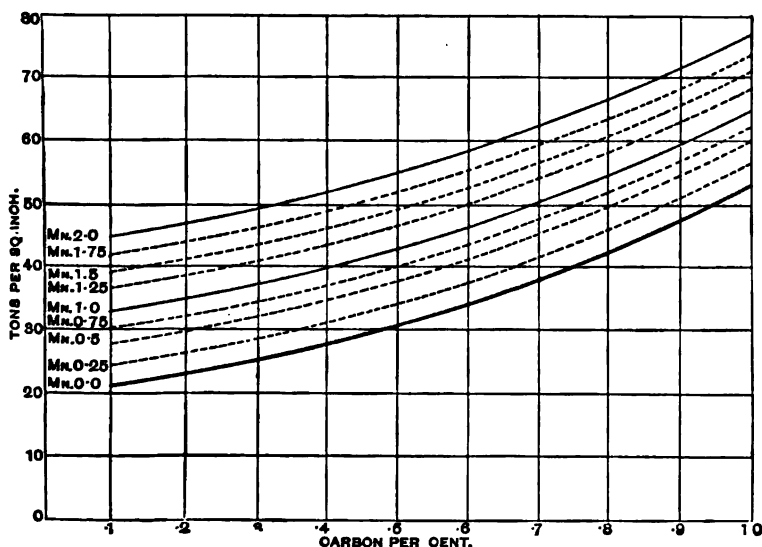


FIG. 10.

Deshayes considers that the modulus of elasticity of all kinds of steel is constant, provided that they have been subjected to identical thermal treatment, and it is safe to conclude that the effect of varying proportions of carbon, within the limits which constitute steel, is probably very slight.

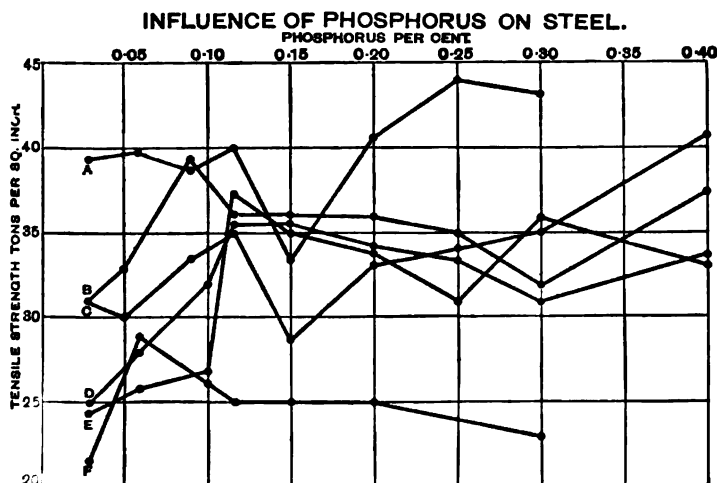
It is difficult to describe briefly the effect of small quantities of manganese on the mechanical properties of carburised iron. Its presence certainly tends to make steel castings sound.

If the effect of the simultaneous presence of manganese and carbon is required to be determined, the vertical line must be prolonged until it cuts the particular curve (Fig. 10) indicating the percentage of manganese in question. The foregoing remarks with regard to the action of manganese in the presence of carbon, are only true with amounts of manganese not exceeding 2 per cent. Further additions of manganese give remarkable results. Although steel, if it may be so termed, containing 4 to 6 per cent. of manganese, and less than 0.5 per cent. of carbon, is so brittle that it can be powdered under a hand-hammer, yet by adding twice this amount of manganese, a return in strength is effected; and Hadfield* thus obtained the remarkable substance known as manganese steel. With about 9 to 10 per cent., a cast bar, $2\frac{1}{2}$ inches square, can be bent considerably out of the straight without breaking. The increase in strength continues up to about 15 per cent., when a decrease takes place in actual toughness, though not in transverse strength, and after about 20 per cent. is passed, a rapid decrease again takes place. The singular point connected with these alloys is that they soften by rapid cooling, the very process which hardens ordinary steel, and conversely they recover their hardness by heating to bright redness. Manganese steel, of the best composition, with about 14 per cent. of manganese, and not more than 1 per cent. of carbon, is made very strong and tough by quenching from a white heat. It is free from blow-holes, and rolls and forges well; but it is so very hard that it is extremely difficult to work in the cold. Its electrical resistance is thirty times that of copper and eight times that of wrought iron, and for practical purposes it may be regarded as wholly unmagnetisable.

The influence of phosphorus and of silicon on iron comes next in importance to that of carbon and manganese. Taking the former element first, the diagram (Fig. 11), in which results given by Mr. Howe have been freely used, shows in a very general way the effect on the tensile strength of steel produced by phosphorus in the presence of amounts of carbon varying from 0.05 per cent. (line F) to 0.4 per cent. (line A). It is well known that phosphorus makes iron "cold-short," and it is now admitted that the presence of this element tends to increase the tensile strength of iron. Indeed, if the carbon be kept very low, a small quantity of phosphorus, the presence of which would formerly have been considered highly dangerous, is not viewed with disfavour even in rails.

* *Journ. Iron and Steel Inst.*, No. 11. (1888), p. 41. This contains an excellent bibliography of the subject.

It is certain that phosphoric iron and steel is very fragile when subjected to suddenly applied stresses, or, in other words, to "shock." Phosphorus usually increases the limit of elasticity of iron, especially in the presence of carbon.



PERCENTAGE OF CARBON.

A	0.40 to 0.50
B	0.30 to 0.40
C	0.25 to 0.30
D	0.20 to 0.25
E	0.10 to 0.15
F	0.05 to 0.10

FIG. 11.

It is very difficult to estimate the influence of silicon. It is known that the addition of silicon to molten steel is useful, as it prevents the formation of "blow-holes" in the solidifying mass. Probably the silicon acts by prolonging the solubility of gas in iron until the metal has actually set. The presence of silicon certainly appears to facilitate the separation of graphitic carbon from iron. Mr. T. Turner,* of the Mason College, Birmingham, a former student of the author's, has done excellent work by studying the action of silicon on pig-iron and steel, and his

* *Journ. Chem. Soc.*, 1885, p. 577 and p. 902.

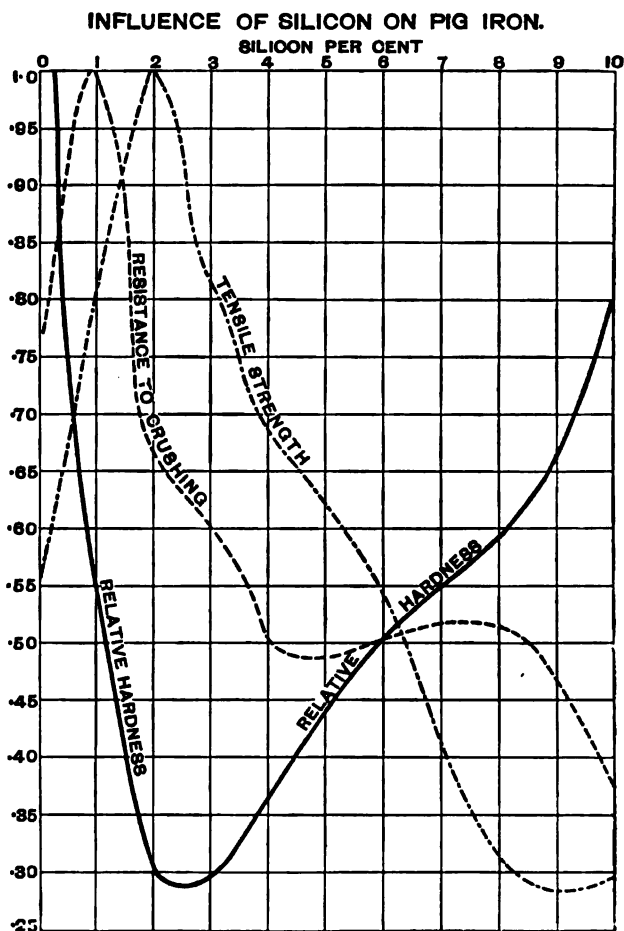


FIG. 12.

results have been conveniently condensed by F. Gantier,* from whose paper the diagram (Fig. 12) has been adapted. The maximum result obtained on the series of samples for each kind of resistance has been taken as unity, and the ordinates are expressed as fractions of this maximum. The datum line of the diagram would, however, fall below the limits of the page.

The chief point of interest is that in pig-iron the maximum resistance to traction (tensile strength), to bending, and to crushing is attained with proportions of silicon varying between 1.5 and 3 per cent. Metal containing between 2 and 3 per cent. of silicon appears to be softer than the rest of the series, whilst the maximum resistance to crushing stress is attained with less than 1 per cent. of silicon. It should be added that the samples of pig-iron examined contained 1.81 to 2.23 per cent. of carbon, and that in the samples rich in silicon the carbon was mainly present in the graphitic state. These also contained about 0.3 per cent. of manganese and a small quantity, about 0.04 per cent., of sulphur.

The results of an elaborate series of mechanical tests by Mr. R. A. Hadfield † on silicon steel in its forged state gave results which are plotted in the accompanying diagram (Fig. 13). In this, the upper pair of curves show the results of tensile tests in tons per square inch, and the lower pair of curves show the results of elongation tests expressed in percentages. Apparently silicon, up to 1.5 or 1.75 per cent., added to iron, although increasing the elastic strength, and raising the tensile strength, does not impair ductility. After this, however, the further increase of tensile strength noticed is only obtained with a serious loss of ductility. There appears to be no sharp line of demarcation, but when 1.5 to 2 per cent. is exceeded, further slight increases cause great changes in the characteristics of the material. In this respect, therefore, its action rather resembles that of carbon than that of manganese, of which larger amounts are required to effect similar changes.

In the case of mild steel, it would appear that the presence of silicon increases the tensile strength, but lowers the elastic strength. ‡ It will be evident, however, from the diagram (Fig. 13) that when the amount of silicon in mild steel exceeds 2 per cent., the extensibility of the material rapidly diminishes.

It should be borne in mind that larger additions of silicon

* *Bull. Soc. de l'Ind. Min.*, vol. iii. (1889), p. 91. See also paper read at the Metallurgical Congress, Paris, 1889.

† *Journ. Iron and Steel Inst.*, No. ii. (1889), p. 222.

‡ *Report Brit. Assoc.* 1888, p. 69.

do not cause a return of strength, which is so remarkable in the case of manganese steel. Silicon steel is, moreover, still magnetic with considerable percentages of silicon, and is in this respect unlike both manganese and nickel steels.

Hopkinson states that the electrical resistance of silicon steel is about six or seven times that of pure iron, and Hadfield has recently shown that the influence of silicon closely resembles that of aluminium.

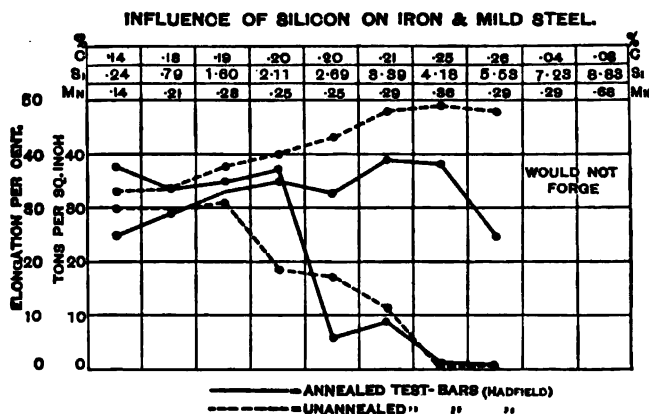


FIG. 13.

The influence of tungsten is remarkable. Its presence causes steel to be very hard, and, as Howe points out, although weight for weight, tungsten probably does not increase the hardness of steel as much as carbon, and perhaps not as much as chromium, yet steel may contain a much larger percentage of tungsten—at least 10 per cent—than of carbon, without losing its property of being forged.

Tungsten steel is very fragile to shock, and, as might be anticipated, its extensibility is very low.

Formerly, it was supposed that the presence of copper was prejudicial to steel; but it has been urged that the deleterious effects observed arose from the presence of small quantities of sulphur with which the copper was associated, and not from the copper itself. Dr. E. J. Ball and Mr. A. Wingham* have shown, by some experiments conducted in the author's laboratory, that the presence of copper materially increases the tensile strength of steel. The results of their experiments are shown in the diagram

* *Journ. Iron and Steel Inst.*, No. i. (1889), p. 123.

(Fig. 14), in which the tensile strength of cupriferous steel is compared with a normal curve for carbon steel, the tensile strength of which is indicated by the dotted line.

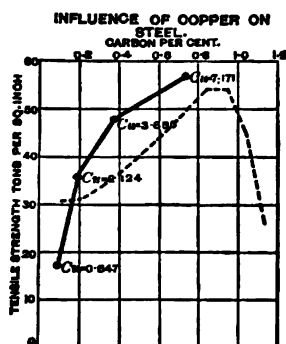


FIG. 14.

ability is as rapidly diminished. Amounts of nickel varying from 8 to 15 per cent. appear to produce such intense brittleness that it is not possible to submit the material to the ordinary mechanical tests. The effect of amounts of nickel exceeding 15 per cent. is so evident from the diagram that no description is necessary. It is singular, however, that a rapid rise in extensibility should be produced by adding some 20 per cent. of nickel to iron, especially as the limit of elasticity of this material appears to be greatly reduced by annealing.

A sample of nickel steel wire, containing about 25 per cent. of nickel, was examined by Dr. J. Hopkinson.† When heated to over 500°, and then cooled either rapidly or slowly, it lost its magnetic properties, which are, however, restored by cooling it to some point below 0°.

Until quite recently,‡ the influence of aluminium had not been systematically studied. There is no doubt that the presence of a small quantity of aluminium, 0.1 to 0.2 per cent., considerably increases the fluidity of carburised iron. Indeed, it has been urged that its presence lowers the melting point of steel by some 200°. This is, however, not proven, and is improbable, but the remarkable fluidity of cast steel containing aluminium may be due to the fact that the aluminium serves to eliminate the oxygen present as oxide of iron.

* *Journ. Iron and Steel Inst.*, No. 1. (1889), p. 45.

† *Proc. Roy. Soc.*, vol. xlvii. (1890), p. 23.

‡ *Trans. Amer. Inst. Min. Eng.*, 1890, p. 835.

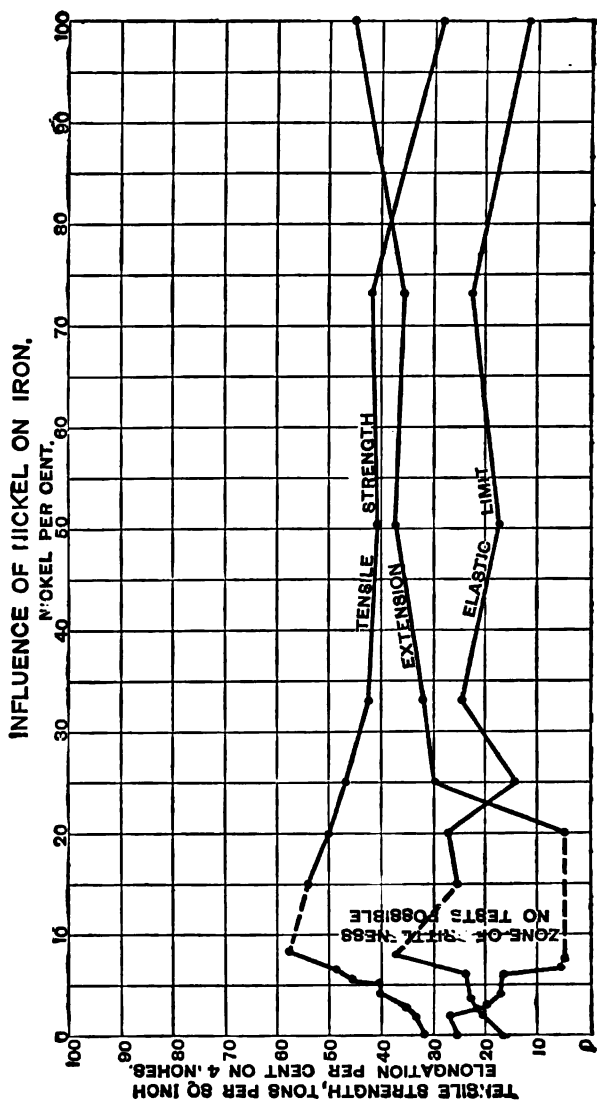


Fig. 15.

The presence of 0.1 to 0.2 per cent. of aluminium hardens steel; but, on the other hand, the metal may be rendered very soft and extensible by annealing. The presence of aluminium appears, as in the case of silicon, to determine the separation of carbon in the graphitic form.

Mr. F. W. Harbord, a former student of the author's, has shown* that the presence of arsenic, even in minute quantities, is very prejudicial to the qualities of the iron.

The alloys of iron and chromium have been specially studied by M. Brustlein,† Director of the steelworks of J. Holtzer & Co., at Unieux, France. Very variable proportions may be combined with iron, the maximum appearing to be 82 per cent. With this material chromium steel may be prepared. The influence of chromium on steel is to increase its tensile strength and its resistance to fracture by impact. Chromium steels are, however, difficult to work hot. Steel with 2 per cent. of chromium is somewhat hard to cut in the cold, and when a mass is hardened in the usual way by quenching, the hardness penetrates more deeply than in the case of steel of the same degree of carburisation. There is, moreover, some difficulty in working these steels occasioned by the tendency of the chromium to oxidise and form slag. They consequently weld with difficulty.

Mr. Hadfield has also studied the effect of aluminium‡ and chromium§ on steel, and his results are shown in Figs. 154 and 155. As regards the influence of aluminium, he finds that successive additions of aluminium, amounting in all to 5.6 per cent., tend to raise the tenacity of the steel, as is shown by the middle curve Fig. 154. The first additions up to 1.6 per cent. lower the elastic limit (see lowest curve), while subsequent additions raise it. The elongation (upper curve) appears to be diminished, whether the test pieces be annealed or not.

In the case of chromium it should be remembered that there is always the simultaneous presence of carbon, but the effect of chromium, up to 5 per cent., increases the tenacity greatly, as is shown by the upper dotted curve, Fig. 155; but further additions lower it. The elastic limit, in unannealed specimens, is also raised at first, as is shown by the upper continuous curve, and afterwards diminished. The lower dotted curve represents the tensile strength of annealed test pieces. In annealed bars, although the tenacity is raised by the presence of chromium, the effect on the elastic limit is but slight (see lower continuous curve). The elongation is in all cases diminished by the presence of chromium. The melting points of chromium steel vary from

* *Journ. Iron. and Steel Inst.*, No. i. (1888), p. 183.

† *Bull. Soc. de l'Ind. Min.*, vol. iii. (1889), p. 1.

‡ *Journ. Iron and Steel Inst.*, No. ii. (1890), p. 161.

§ *Ibid.* No. ii. (1892), p. 49.

1325° C. to 1330°. Steel containing the same amount of carbon as the specimens, but no chromium, would melt at about 1420°. Chromium, in the absence of carbon, does not appear to materially harden steel, but there is no doubt that the carbon-chromium-iron alloys are very hard. As regards hardening by quenching chromium steel, the presence of chromium does not appear to exert a marked influence. On the other hand, alloys of iron containing 5 per cent. chromium and 0.77 per cent. of carbon are very hard after slow cooling.

The influence of sulphur on iron is very marked. This element has the effect of making iron exceedingly brittle at a red heat and

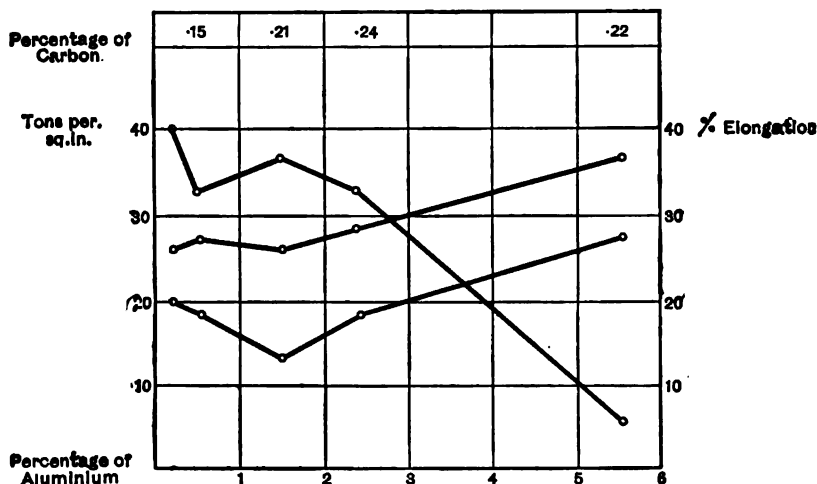


FIG. 15a.

of destroying its welding power. As a rule, the action is most marked at a dull-red heat. Manganese counteracts the prejudicial action of sulphur.

To take copper as an example instead of iron, the influence of tin on this metal, as far as mechanical properties are concerned, is shown by the accompanying diagram (Fig. 16), in which the upper curves represent the tensile strengths as determined by Mallet and by a Board of investigators appointed by the Government of the United States.* It may be sufficient to state that the addition of tin to copper rapidly lowers its conductivity for electricity, but, as shown by the results obtained by the U.S. Board,

* Report on a preliminary investigation of the properties of the copper-tin alloys. Washington, 1879.

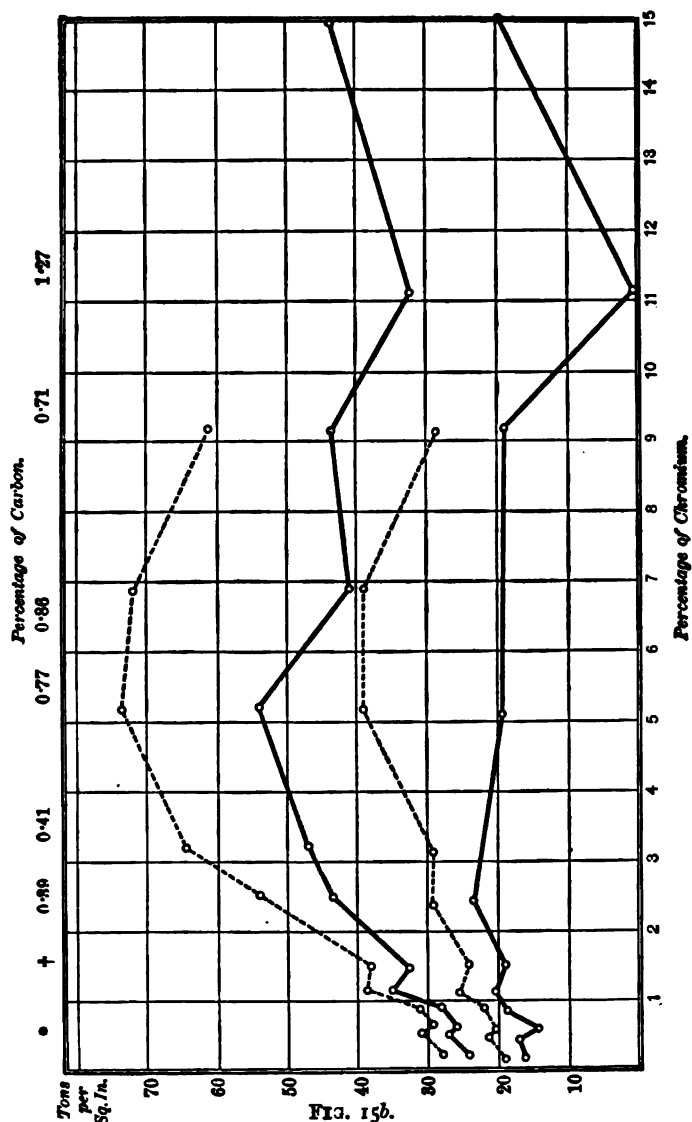


FIG. 15b.

* Percentage of Carbon 0.07, 0.16, 0.14 and 0.12 per cent.

+ " " 0.27 and 0.21.

INFLUENCE OF TIN ON COPPER.

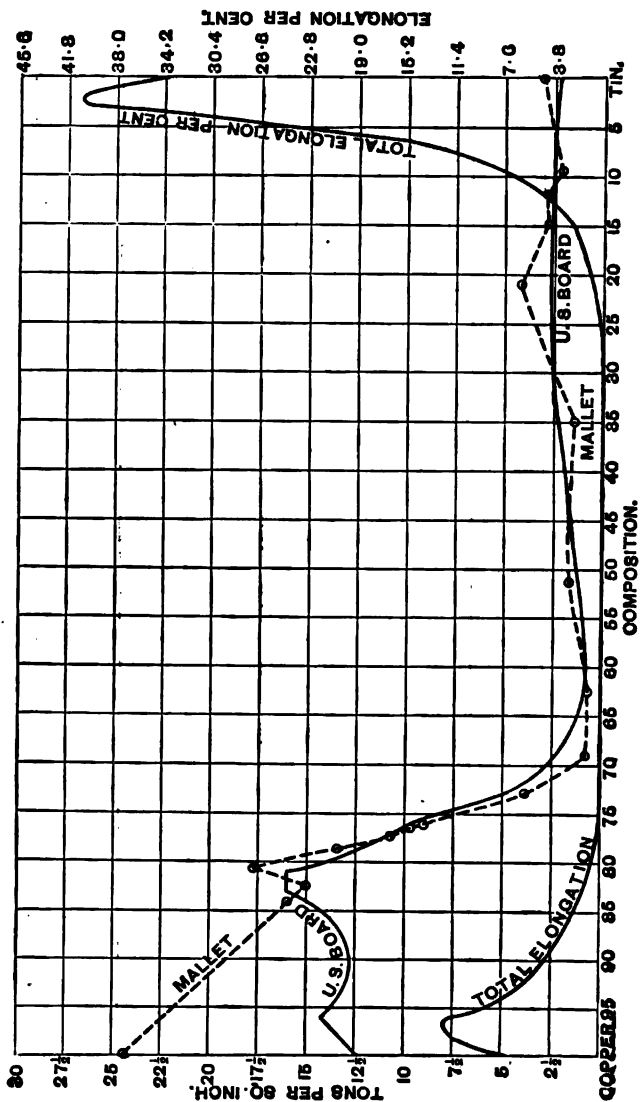


Fig. 16.

increases its strength, the maximum being attained with about 20 per cent. of tin. The entire series of copper-tin alloys is very interesting. Two only appear to be homogeneous, and these correspond respectively to the formulæ SnCu_2 and SnCu_4 . Notwithstanding the comparatively small difference in their composition,

the appearance of the fractured surfaces of these alloys is quite different, the latter being yellowish grey in colour with a mirror-like fracture, whilst the former is blue with a rough fracture. Having a higher specific gravity than the mean of its constituents, the alloy SnCu_2 stands out from the rest of the series.

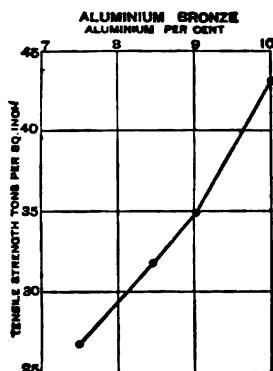


FIG. 17.

square inch, and in castings has a tensile strength of 70,000 to 80,000 lbs. per square inch. This alloy, which was discovered by the late Dr. Percy, closely resembles gold in appearance. The effect of smaller proportions of aluminium on copper is shown in the accompanying diagram (Fig. 17).

In discussing the influence of foreign elements on iron, the terms "cast iron," "wrought iron," and "steel" are used, as this classification is still in general use among engineers. In 1878, however, an international commission at Philadelphia decided to adopt a classification based on the amount of carbon contained in the metal:—

I. *Pig iron* with 2.3 per cent. and more of carbon; melts at a comparatively low temperature (1075° to 1275° C.) and cannot be forged.

a. *White pig iron*; all the carbon is combined with the iron, the compound is very hard, brittle, white, and is made solely for the purpose of being converted into malleable iron.

b. *Grey pig iron*; in which more or less of the carbon is present in the form of graphite. The metal is soft, tough, grey to black, and is used for conversion into malleable iron or for the production of castings.

II. *Steel* with 1.6 to 0.4 per cent. of carbon, melts at 1400° to 1500° C. By sudden cooling of a red-hot mass the hardness is considerably increased.

III. *Weld iron* with less than 0.2 per cent. of carbon, melts at 1600° C. and above. It cannot be appreciably hardened.

The Philadelphia Commission decided that—

1. Every malleable compound of iron, containing the ordinary elements of that metal, which is obtained either by the union of pasty masses of iron or by any process not involving fusion, and which cannot be hardened by the ordinary method, shall be called *weld iron*. This is what has formerly been known as wrought iron.

2. Any analogous compound, which by any cause hardens, shall be called *weld steel*. This has hitherto been termed puddled steel.

3. Every malleable compound of iron, containing the ordinary constituents of that metal, which is obtained and poured in the fused state, but which does not harden by the ordinary methods, shall be known as *ingot iron*.

4. Every compound similar to the last, but capable of hardening from any cause whatever, shall be called *ingot steel*.

Colour.—The colour of metals is influenced by their purity. Thus, iron becomes white by admixture with carbon, silicon, sulphur, phosphorus, and other elements. By the alteration in the colour of a metal it is possible to detect the presence of a very small quantity of impurity, especially in the case of gold.

The lustre of metals is due to their great power of reflecting light. It varies with the purity and the degree of polish of the metal. It is therefore of great use in detecting the presence of impurities, a notable example of this being afforded by copper.

Fusibility.—All metals are fusible. On account of the difficulty experienced in determining high temperatures, only the melting points of the metals that fuse at temperatures below 1000° have been ascertained with absolute accuracy. The melting points of the more important metals are given in the table on pp. 58, 59. Arsenic sublimes at 180°, but it may be fused under the pressure of its own vapour.

When strongly heated, metals pass from a brownish-red to a clear red colour, which gradually increases in luminosity and transparency to a dazzling white. The temperatures corresponding to the different colours have been estimated by Pouillet to be—

Incipient red	525°
Dark red	700°
Incipient cherry-red	800°
Clear cherry-red	1000°
White	1300°
Dazzling white	1500°

On solidifying from a molten state, metals frequently exhibit excrescences due to the expulsion of absorbed gases. This expulsion often occurs shortly before the solidification, and causes a sudden outburst of metal through the surface. In this way silver, when molten, absorbs oxygen, and expels it on solidification. In the case of steel, the evolution of gas continues long after the metal has solidified on the surface.

When a metal passes from the liquid to the solid state, it either does so suddenly, or it passes through an intermediate pasty stage. This fact is occasionally of great metallurgical importance. Thus, white pig iron is more suitable for dry puddling than is grey pig iron, as the former becomes very pasty, whilst the latter does not.

On solidification after melting, metals usually crystallise. Crystallisation also occurs when metals are condensed from a state of vapour or are deposited by the electrolytic decomposition of metallic solutions. Metals most frequently crystallise in the cubic system. This is the case with platinum, gold, silver, copper, lead, and iron, and probably with tin and zinc. Tin also crystallises in the tetragonal system, and the iron-manganese carbide *spiegeleisen* crystallises in the rhombic system. Antimony, arsenic, and zinc crystallise in the hexagonal system, whilst bismuth crystallises in rhombohedra resembling cubes. Tin, zinc, and lead are thus dimorphous—that is, they may be developed according to two systems of crystallisation. The crystallisation of metals is of great importance, as the formation of crystals, due to continued vibration, intense cold, sudden alterations of temperature, or the presence of impurities may render a metal absolutely useless. Crystallisation may serve to indicate the quality of the metal, as in the case of foundry pig iron; to indicate the presence of impurities, as in the case of the film of antimony produced on lead that is refined by steam; and, lastly, to separate metals on a large scale, as is the case in Pattinson's process of de-silverising lead.

Welding is the property possessed by metals, which on cooling from the molten state pass through a plastic stage before becoming perfectly solid, of being joined together by the cohesion of the molecules that is induced by the application of an extraneous

force, such as hammering. This property is exhibited in a marked degree by iron and platinum at a white heat. Welding may also be effected, though to a less degree, when two clean surfaces of metal are brought into intimate contact in the cold.

Metals are good conductors of heat and electricity, and may be arranged in the same order as regards both the conductivity for heat and that for electricity.

Iron, nickel, and cobalt may be rendered magnetic. When a small quantity of carbon has converted the iron into steel, the metal readily retains its magnetism.

Certain metals possess acoustic properties. The sound emitted by metals when struck is greatly affected by the presence of impurities. Thus, in the case of lead, the presence of antimony tends to heighten the sound emitted. Owing, it is supposed, to the sliding of the crystal faces over one another, tin, at ordinary temperatures, and zinc, after heating to 160° , emit a sound when bent.

Properties common to Fluids and Solid Metals.—Réaumur, so long ago as 1713, defined with singular clearness the conditions under which metals prove to be ductile. The relation between the behaviour of solid metals and fluids has long been recognised, not in the sense that atomic motion is common to solids and fluids, but from a wider view, for there is much experimental evidence as to the properties that are common to fluids and solid metals, the characteristics of which, at first sight, seem widely separated. A solid has a definite external form, which either does not change, or only changes with extreme slowness when left to itself, and, in order to change this form rapidly, it is necessary to submit it to a considerable stress. A liquid, on the other hand, can be said to have no form of its own, as it always assumes that of the containing vessel; the mobility of its particles is extreme, its resistance to penetration is very small, and its free surface is always a plane when the mass is left at rest. Then there is the colloid condition, which intervenes between the liquid and crystalline solid state, extending into both, and probably affecting all kinds of solid and liquid matter in a greater or less degree. The colloid, or jelly-like body does present a certain amount of resistance to change of shape. Such a substance is well imitated by a sphere of thin india-rubber partly filled with water. Another illustration is probably afforded by iron and other substances which soften under heat, and may be supposed to assume, at the same time, a colloid condition. Last, there is the gaseous condition of matter.

Metals are usually regarded as typical solids; it is easy, how-

ever, to trace the analogies of their behaviour under certain conditions with that of fluids. The transition from the liquid to the solid state is marked by the same phenomena in the case of many metals, as are observed in certain fluids. For instance, metals on solidifying reject impurities, and exhibit the property of surfusion. This leads up to the relations between solid metals and fluids, and the following list shows the classes in which the properties common to fluids and solid metals may be grouped:—

1. Flow under pressure.
2. Changes due to compression.
3. Absorption of gases.
4. Absorption of liquids.
5. Diffusion.
6. Vaporisation.
7. Surface tension.

Water, on passing from the liquid to the solid state, undergoes a partial purification, the ice first formed being sensibly more free from colouring matter or suspended particles than the water from which it separates.

Many metals on freezing similarly eject impurities. In the case of alloys, saturated solutions of one metal in another appear to be formed, and excess of metal ejected, a fact which was studied with much care by Dr. Guthrie (see p. 69). The prominent facts are perhaps best illustrated by reference to a solidified mixture of copper, antimony, and lead. The results of some experiments conducted, in the laboratory of the Royal School of Mines, by Dr. E. J. Ball * show that when a molten mixture of these metals is solidified, a definite atomic alloy of copper and antimony, which possesses a beautiful violet tint, first forms, and, after saturating itself with lead up to a certain point, ejects the rest of the lead, driving it to the centre of the mass so as to form a sharp line of demarcation between the outer violet circle and the grey centre. It thus presents a direct analogy to the comparatively colourless ice which first forms from coloured water. There is yet another remarkable analogy between the freezing of certain fluids and the solidification of some metals. Water may, as is well known, be cooled down to -8°C . without solidification, but agitation immediately determines the formation of ice, and, at the same time, a thermometer plunged in the water rises to zero. Faraday stated,† in 1858, that fused acetic acid, sulphur, phosphorus, many metals, and many solutions would exhibit the

* *Journ. Chem. Soc.*, vol. liii. (1888), p. 167.

† *Experimental Researches in Chemistry and Physics*, p. 379.

same effect. Tin also may be cooled to several degrees below its solidifying point without actually freezing, and Dr. Van Riemsdijk,* of Utrecht, has observed that a globule of gold or silver, in a fused state, will pass below its solidifying point without actually solidifying, but the slightest touch with a metallic point will cause the metal to solidify, and the consequent release of its latent heat of fusion is sufficient to raise the globule to the melting point again, as is indicated by a brilliant glow which the button emits.

It may be well also to remark incidentally that a minute variation in composition is sometimes sufficient to lower the melting point of a metal or alloy, as is instanced by the addition of $\frac{3}{16}$ per cent. of silicon to standard gold, which then softens in the flame of a candle, or at about the melting point of zinc, 412°C ., although the melting point of standard gold, free from silicon, is 946° (T. K. Rose, in the Author's laboratory).

The result of Raoult's investigations on the lowering of the freezing point of solutions, led him to the conclusion that one molecular proportion of any substance dissolved in 100 molecular proportions of any solvent whatever, lowers the freezing point of that solvent 0.62°C . This had not been tested in the case of solutions of metals in metals, until Heycock and Neville† began an elaborate investigation of the subject. Their research, as far as it has at present been carried, deals, 1st, with the lowering of the freezing points of sodium and tin produced by the addition to them of certain other metals, and, 2nd, with the molecular weights of metals when in solution. The results of their experiments when compared with the empirical laws of Coppet and Raoult may be briefly stated as follows:—

They are in accordance with the law "that for moderate concentration the fall in the freezing point is proportional to the weight of the dissolved substance present in a constant weight of solvent." By making the assumption, that the molecule of zinc, or of mercury, is monatomic when in solution in tin, they confirm the second law, "That when the falls produced in the same solvent by different dissolved substances are compared, it is found that a molecular weight of a dissolved substance produces the same fall whatever the substance is." But the third law which states, "That if a constant number of molecular weights of the solvent be taken, then, the fall is independent of the nature of the solvent," they found to be probably incorrect, and theoretical considerations indeed would lead us to expect this. In the case of silicon in standard gold which has just been mentioned, a long semi-fluid stage appears to be set up, the metal may contain solidified

* *Ann. de Chim. et de Phys.*, t. xx. (1880), p. 66.

† *Journ. Chem. Soc.* vol. lv. (1889), p. 666; vol. lvii. (1890), pp. 376 and 656. For further experiments by the author, see p. 169.

particles, and yet be sufficiently fluid to flow readily; this phenomenon has not yet been fully investigated.

In a research of much interest, Ramsay * has determined the molecular weight of a number of metals by Raoult's vapour pressure method—that is, he ascertained the depression of the vapour pressure of the solvent, produced by a known weight of dissolved substance, and he finds that although sodium behaves irregularly, yet “it would appear legitimate to infer that in solution, as a rule, the atom of a metal is identical with its molecule, as the physical properties of those metals which have been vaporised would lead us to suppose.”

Now to pass to solid metals. It is the common experience that a counterfeit shilling, consisting principally of lead, does not “ring” when thrown on a wooden surface. In 1726 Louis Lemery observed that lead is, under certain conditions, almost as sonorous as bell-metal.† He communicated the fact to Réaumur, who, being much struck by it, investigated the conditions under which lead becomes sonorous, and submitted the results to the French Academy.‡ He pointed out that, in describing a body which is not sonorous, it is usual to say that it is as “dull as lead,” an expression which has become proverbial. Nevertheless, he adds, under certain conditions, lead has a property both novel and remarkable, for it emits surprisingly sharp notes when struck with another piece of lead. He showed that it was necessary that the lead should be formed by casting into a segment of a sphere—that is, mushroom-shaped. The lead must be free from prominences, and must be neatly trimmed. The effect is less marked if the lead be very pure than if ordinary commercial lead be used, but it is only a question of degree. Réaumur showed that the sonorous lead might be rendered dull by hammering it. His remarks have been overlooked in late years. He was led to the belief that in cast lead there must be an arrangement of the interior of the mass which the hammer cannot impart, because lead fashioned by hammering into the same form as the sonorous cast mass is dull, and, more important still, he held that the fibrous and granular structure of the lead is modified in a manner which makes it probable that the sound is due to the shape of the grains and to the “way in which they touch each other;” further, the blows of the hammer not only change the arrangement of the fibres, but

* *Journ. Chem. Soc.*, vol. lv. (1889), p. 521. See also Tammann, *Zeit. für physikal. Chemie*, 1889, p. 441.

† Hofer, *Histoire de la Chimie*, ii. p. 383.

‡ *Histoire de l'Académie Royale des Sciences, Année 1726* [vol. for 1728, p. 243].

they alter the shape of the grains; "the round grains are rendered flat, they are compelled to elongate and fill the interstitial spaces which previously existed between them. The particles are no longer free to vibrate; hence the lead is dull." These facts acquire additional interest if they are compared with the observations in Professor Osborne Reynolds' paper on "Dilatancy in Granular Matter." Réaumur's description shows that he fully appreciated the theoretical importance of the kind of facts depending on the transfer of metallic matter from one position to another, which we now consider to be characteristic of the "flow" of metals; at any rate, Lemery's experiment may be made the starting point of the remarks which follow.

A solid may be very brittle, and may yet, if time be given to it, flow from one point to another. A stick of sealing wax, or even of glass, supported at its ends, in a few weeks bends at the ordinary atmospheric temperature, although at any given point of its flow it would have been easy to snap it with a slight application of force. A tuning-fork may be made from pitch, which will nevertheless subside into a shapeless mass at the ordinary temperature. A much thinner strip of pure lead of the same breadth as the sealing wax also bends at the ordinary temperature with its own weight, the ends being supported. Lord Kelvin has, however, pointed out that a gold wire, sustaining half the weight which would actually break it, would probably not rupture in a thousand or even a million years—that is to say, there would be no "flow" ending in disruption; if, however, force be suitably applied, metals will flow readily. First, examine the case of a metal under force applied so as to compel it to flow through a hole, as it points to the analogy of an ordinary viscous fluid. If a vessel (1, Fig. 18) provided with a cylindrical hole in its base be filled with lead, the lead will, at the ordinary pressure, remain there, but if extra pressure be applied the lead will prove by its behaviour that it is really a viscous solid, as it flows readily through the orifice; the end of the jet is rounded, and, as has been shown by the beautiful researches of the late M. Tresca, of Paris,* all the molecules which compose the original block place themselves in the jet absolutely as the molecules of a flowing jet of a viscous fluid would. If the metal has a constant "head," as it would be termed in the case of water—that is, if the vessel be kept filled with solid lead up to a certain level—then

* These researches extend through a long series of memoirs; those relating to the flow of metals are well summarised in the *Proc. Inst. Mech. Engineers*, 1867, p. 114, and in the Report of the Science Conferences held in connection with the Loan Collection of Scientific Apparatus (Physics and Mechanics), London, 1876, p. 252.

there will be a continuous stream, the length depending on the constancy with which the "head" and the pressure are maintained. If, on the other hand, the "head" is diminished so that nearly all the solid lead has been allowed to flow away (2, Fig. 18), there is a folding of the jet, and vertical corrugations, exactly such as would characterise the end of the flow of certain other viscous fluids, and finally the jet forms a distinct funnel-shaped tube concentric with the jet. It is also seen that, when the formation of these cavities takes place, the jet is no longer equal to the full diameter of the orifice, as shown in 2, Fig. 18, the formation of the contracted vein is manifest, and the new analogy is thus obtained between the flow of solids and of liquids.

In punching a disc from a solid plate of metal supported by a die-plate (4, Fig. 18), as in the operation of coining, the portion cut

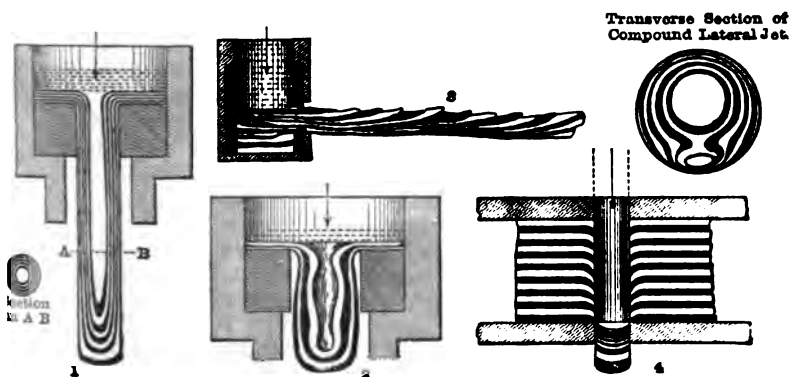


FIG. 18.

out proves to be thinner than the plate from which it has been removed. Since the density of a metal is not increased by pressure except by the obliteration of pores, as has already been stated, it follows that the metal must have flowed in a plastic state laterally from the disc into the plate, the remaining metal becoming so thin that its resistance to shearing is less than the pressure on the punch.

In 3, Fig. 18, the effect is shown of a compound jet of lead flowing through a lateral orifice in a cylindrical vessel.

In the case of planing surfaces of metals by cutting tools, similar effects may be traced, and it is interesting to compare the flow of metal in 4, Fig. 18, which represents the penetration of a

cutting tool through a plate of metal, with the flow of metal under the action of a tool used for planing (Fig. 19). In this case the lines of flow are made evident by the deformation of lines traced vertically on the side of the block of metal submitted to the tool. The shifting of the material and the connection of the lines, F, in the shaving with those, E, of the original block, will be evident from the diagram. Every artificer knows how complicated in form the shavings may be, and varied problems relating to their production have been studied by M. Tresca.*

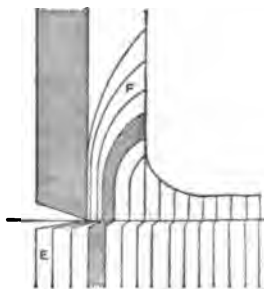


FIG. 19.

The application of this fact, that solid metals flow like viscous fluids, is of great importance in industry, and the production of complicated forms by forging or by rolling iron and steel and other metals entirely depends on the flow of the metal when suitably guided by the artificer. The lines of flow in iron may be well shown by polishing a surface of the metal, and by submitting it to the action of a solution of mercuric chloride, which etches the surface, or, better, to the slow action of chromic acid solution, the result in either case being, that any difference in the hardness of the metal or in the chemical composition, or want of continuity, caused by the presence of traces of entangled slag, reveals the manner in which the metal has flowed. The sketches illustrate the direction of flow in the following cases. Fig. 20 is a section of a forged cross-head, and Figs. 21, 22 are sections of rails.

The experiments of M. Tresca were not made on "cinder-free" metal; it is therefore interesting to compare the etched section of the old rail, Fig. 21, the result of the complicated welding of puddled iron, with a basic-Bessemer rail, rolled from steel which has been cast, and which is therefore free from entangled slag. Fig. 22 represents a section of such a rail.

A very striking illustration of the importance of the flow of metals, when used in construction, is afforded by some observations of Sir B. Baker in a paper on the Forth Bridge.† He says: "If the thing were practicable, what I should choose as the material for the compression members of a bridge would be 34- to 37-ton steel, which had previously been squeezed endwise, in the direction of the stress to a pressure of about 45 tons per

* *Mémoires de l'Académie des Sciences*, vol. xxvii., No. 1, 1880.

† *Journ. Iron and Steel Inst.*, 1885, p. 497.

square inch, the steel plates being held in suitable frames to prevent distortion." He adds: "My experiments have proved that

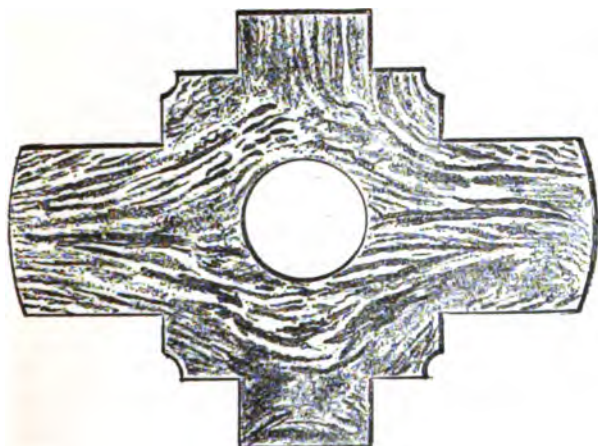


FIG. 20.

37-ton steel so treated will carry as a column as much load as 70-ton steel in the state in which it leaves the rolls—that is to say,



FIG. 21.



FIG. 22.

not previously pressed endwise. . . . At least one-half of the 42,000 tons of steel in the Forth Bridge is in compression, and the same proportion holds good in most bridges, so the importance of gaining an increased resistance of 60 per cent. without any sacri-

fice in the facility of working, and safety, belonging to a highly ductile material can hardly be exaggerated."

The very ancient mechanical art of striking coin is wholly dependent on the flow of metals. There is a popular belief that the impression imparted to discs of metal during coinage is merely the result of a permanent compression of the metal of which the disc is made. Striking a coin, however, presents a case of moulding a plastic metal, and of the true flow of metal, under pressure, into the sunken portions of the die. A medal struck from a series of discs will serve to show, when the discs are separated, the way the metal flows into the deepest portion of the die. If the alloy used be too hard, or if the thickness of the metal required to flow be insufficient, the impression will always be defective, no matter how many blows may be given by the press.

If one side of the coin be ground away, so as to leave a flat surface, and if the disc be then struck between plain polished dies surrounded by a steel collar, so as to prevent the escape of the metal, the impression on the disc will be driven through the thickness of the metal, and will then appear on both sides. In industrial art the property of flow of metals is very important. The "spinning" of articles in pewter is a familiar instance.

The production of complicated forms, like a jelly mould, from a single sheet of copper under the combined drawing and compressing action of the hammer is a still more remarkable case.

The flow of metals is illustrated very curiously in one phase of Japanese art metal-work, to which reference will be made subsequently.

The flow of metals when submitted to compression has hitherto been alone considered, but the effect of traction has also been examined, for when a viscous metal such as iron or soft steel is submitted to stress by pulling its ends in opposite directions, it stretches uniformly throughout its length, and the metal truly flows when the yield point is reached. The limit of elasticity of a solid body marks the moment at which the body begins to permanently stretch, under the influence of the longitudinal stress to which it is submitted. There are many materials which do not stretch sensibly when their limit of elasticity is reached; in very hard steel, for instance, the breaking point and the limit of elasticity practically coincide. Further, it must be observed that every minute variation in composition is sufficient to change the property of a body, and to cause what was a viscous body to break close to the limit of elasticity.

The particles of a metallic powder left to itself at the ordinary

atmospheric pressure will not unite ; by "augmenting the number of points of contact in a powder" the result may be very different. The powders of metals may weld into blocks, as will subsequently be described, and it will be seen that experiments on the compression of finely divided metals afford important evidence as to the relation between solid metals and fluids. Faraday discovered, in 1850, that two fragments of ice pressed against each other will unite, their tendency to union being considerable when the fragments are near their melting point. Ice owes its movement, in glaciers, not to viscosity, but to regelation, and the union of fragments of ice under compression is also due to regelation. The facts which have been appealed to, and the theories which have been formed, respecting the regelation of ice, are well known ; it may, however, be observed that bismuth, like ice, expands on solidifying, and though Faraday failed to establish the existence of a property similar to regelation in bismuth, Wrightson has satisfied himself, by experimental evidence, that regelation exists in bismuth. In explaining Spring's results (p. 65) there is this difficulty : the union of the particles of the metals, cannot, in all cases, be due to viscosity, because viscous bodies are always capable of being stretched, and we find the welding taking place between the compressed powders of bodies, such as zinc and bismuth, which, when submitted to traction, will not stretch. Spring therefore asks, "Is it possible that regelation may have something to do with the union of the powders ?" and he urges, "Is it safe to conclude that regelation is peculiar to ice alone ?" "It is difficult to believe," he adds, "that in the large number of substances which Nature presents to us, but one exists possessing a property of which we can find only minute traces in other bodies. The sum of our chemical and physical knowledge is against such a belief, and therefore the phenomenon of regelation may be pronounced in ice without being absolutely wanting in other bodies. To ascertain whether this is so, it is necessary to submit other bodies to the conditions under which the phenomenon can be produced." "What," he asks, "are these conditions ?" and he answers, "The pressure supported by the body, a certain degree of temperature, and time."

Both Helmholtz and Tyndall have shown that when the pressure is weak the regelation of ice is effected slowly. Spring points out that nitrate of sodium and phosphate of sodium, in powder, left to themselves in bottles, become coherent, and if the coherence in these and other chemical compounds is but weak, it is simply because the points of contact between the particles of powder are but few. If, on the other hand, metallic or other powder be submitted to strong compression, the spaces between the fragments

become filled with the débris of the crushed particles, and a solid block is the result. Finally, it may be urged that this union of powders of solid metals under the influence of pressure—that is to say, the close approximation of the particles—can be compared to the liquefaction of gases by pressure. At the first view this comparison may appear rash or strained, but it is not so if the views of Clausius on the nature of gases and liquids be accepted. In a gas the molecules are free, but if by pressure at a suitable temperature the molecules are brought within the limit of their mutual attraction, the gas may be liquified, and under suitable thermal conditions, solidified. The mechanical pulverisation of a metal merely detaches groups of molecules from other groups, because the mechanical treatment is imperfect, but the analogy between a solid and a gas has, in this sense, been established; filing coarsely gasifies the mass, but pressure solidifies it.

It is possible that in some of the compressed metallic blocks, the particles are not actually united by the pressure, which may, nevertheless, develop the kind of “mutual attraction” contemplated by Lord Kelvin as existing between two pieces of matter at distances of less than 10 micro-millimetres.

Occlusion of Gases.—With reference to the absorption of gases by metals, it may be sufficient to point out that Sainte Claire-Deville and Troost discovered that hydrogen would pass through a plate of platinum, prepared from the fused metal or through iron, at a red heat; and it was well known that molten silver had the power of absorbing many times its own volume of oxygen. In Deville's experiments a new kind of porosity was imagined, more minute than that of graphite and earthenware, an intermolecular porosity due entirely to dilatation. Graham * showed that when gas penetrates the substance of the metal there is previous absorption and possibly liquefaction of the gas. Since his time it has been abundantly recognised that the presence of an element which is capable of re-appearing with the elastic tension of a gas must materially affect the mechanical properties of a metal. Palladium is known to possess the power of occluding gas—hydrogen—in the most marked degree. By slow cooling from a red-heat in an atmosphere of hydrogen, palladium foil or wire occludes no less than 900 volumes of hydrogen. Similarly, gold is found to occlude, that is, *retain when solid*, 0.48 of its volume of hydrogen and 0.2 of its volume of nitrogen, silver occludes 0.7 of its volume of oxygen, and wrought copper occludes 0.306 volume of hydrogen.

It is, however, in relation to the metallurgy of iron that the

* *Proc. Roy. Soc.*, vol. xvi. p. 422; vol. xvii. p. 212, and p. 500; *Trans. Roy. Soc.*, 1886, pp. 399-439.

occlusion of gases is of importance. It is well known that at the conclusion of the Bessemer process, oxygen from the air blown through the metal becomes intimately associated with iron; but the manner in which the oxygen is held, whether as oxide or as dissolved gas, appears to be still obscure, though Müller* has given strong evidence in support of the view that gases are dissolved in iron. One thing is certain, that the oxygen may readily be removed from the iron by the action of manganese. Hydrogen is usually present in iron, chiefly as gas, sometimes as ammonia,† and in certain cases probably in some non-gaseous state. It does not appear to be in strong chemical combination, as it can easily be expelled. This may happen on solidification of the metal, by heating in vacuo, or by the action of a drill, which appears to release entangled or loosely-held hydrogen. The escape of gas can be prevented by increasing the pressure during solidification, and by the addition, before solidification, of silicon, manganese, or aluminium. The hydrogen probably remains in the cold iron after it is solidified. Cailletet‡ extracted from electrolytic iron, in which the metal probably exists in a distinct molecular form, nearly 250 times its volume of hydrogen by heating in vacuo. Graham proved that carbonic oxide is dissolved by iron, and that that gas probably plays an important part during the conversion of iron into steel in the ordinary process of cementation. It is certain that the presence of silicon and manganese appears to enable the iron to retain carbonic oxide, as well as hydrogen and nitrogen, in solution.

Another analogy between metals and fluids is presented by the power which certain solid metals possess of taking up fluids, sometimes with a rapidity which suggests the miscibility of ordinary fluid substances. In reference to this, an interesting paper was published, so long ago as 1713, by the Dutch chemist Homberg,§ "On Substances which Penetrate and which Pass Through Metals, without Melting Them." He enumerates several substances which will pass through the pores of metals without disturbing the particles, and he points out that mercury penetrates metals without destroying them. The rapidity with which mercury will pass through tin is remarkable. A bar 1 inch wide and $\frac{1}{2}$ inch thick will be penetrated by mercury in thirty seconds, so that it breaks readily, although before the addition

* *Iron*, 1883, vol. xxi. p. 115, and vol. xxii. p. 244; 1884, vol. xxiii. p. 161.

† Recognised by many observers; notably by Regnard, *Comptes Rendus*, vol. lxxiv. (1877), p. 260.

‡ *Comptes Rendus*, vol. lxxx. (1875), p. 319.

§ *Mém. de l'Acad. Royale des Sciences*, 1713 (vol. for 1739, p. 306).

of the mercury the bar would bend double without any sign of fracture.

With regard to the vaporisation of solid metals, Demarçay* has shown that in *vacuo* metals evaporate at much lower temperatures than they do at the ordinary atmospheric pressure, and he suggests that even metals of the platinum group will be found to be volatile at comparatively low temperatures. Merget† has shown that the solidification of mercury by extreme cold does not prevent the solid metal evaporating into the atmosphere surrounding it.

In relation to surface tension there is an interesting property belonging to a hard drawn rod or thick wire of 13-carat gold, the gold being alloyed with silver and copper in the following proportions:—

Gold	54.17
Copper	33.33
Silver	12.50
								<hr/>
								100.00

If such a rod be touched with a solution of chloride of iron, or certain other soluble chlorides, it will, in a short time, varying from a few seconds to some minutes, break away, the fracture rapidly extending for a distance of some inches.

The last property to be considered is diffusion. The author has shown that in the case of molten metals the interdiffusion may be extremely rapid. In regard to solid metals, some experiments conducted by Abel prove that carbon can pass from a plate of richly carburised iron to one of iron free from carbon against which it is tightly pressed. This passage of carbon appears to take place at the ordinary temperature, and it is difficult to explain the transference of matter without admitting the presence of some action closely allied to the diffusion of liquids.

These facts afford additional evidence as to continuity in the properties of all kinds of matter, and serve as a connecting link with the work of the past, the importance of which is too often overlooked.

This chapter may fittingly conclude with a table of the physical constants of metals.

* *Comptes Rendus*, vol. xcv. (1882), p. 183.

† *Ann. de Chim. et de Phys.* (4), vol. xxv. p. 121.

For Table of Physical Constants, see next page.

Notes to the Table of Physical Constants (pp. 58, 59).—For melting points the student must refer to the *Physikalisch-chemische Tabellen*, by Drs. Landolt and Börnstein, Berlin, 1883, *p. 81, and to papers by Violle (*Comptes Rendus*, vol. lxxxix. (1879) p. 702), and by Pictet (*ibid.*, vol. lxxxviii. (1879) pp. 855, 1315). The atomic weights and atomic volumes are those given in Lothar Meyer's *Modern Theories of Chemistry*, London, 1888. With regard to electrical conductivity, it is usual in this country to employ pure copper as a standard of reference for industrial purposes. For scientific purposes, it has been usual to refer to pure silver, and to assign to it the value 1000. In view, however, of the fact that it is very difficult to obtain silver of absolute purity, and that the conductivity varies greatly with the thermal and mechanical treatment to which the metal has been subjected, it has been considered better to adopt mercury at 0° as the standard metal, its electrical conductivity being taken as unity. The figures given in the last column of the table may be converted into a series in which silver would be 100, by simply multiplying by 1.75.

NOTE.—While this volume is passing through the press, Professor Dewar stated, in a lecture delivered at the Royal Institution Jan. 19, 1894, that when metals are exposed to the very low temperature of -180°C ., the tenacity is greatly increased: for instance, steel, which breaks with a stress of 34 tons per square inch, is nearly double as strong at -180° . The strength of German silver is also nearly doubled. The elongation of the steel does not appear to be changed by this very low temperature.

* There is a later edition of these tables (1893).

PHYSICAL CONSTANTS OF METALS.

		Atomic Weight.	Atomic Volume.	Specific Gravity.	Specific Heat.	Melting Point.	Co-efficient of linear Expansion.	Thermal Con-ductivity.	Electrical Con-ductivity.
—									
ALUMINIUM . . .	Al	27.00	10.6	2.56	0.212	° C. 625	0.0000231	Ag = 100. 31.33	Hg at 0° = 1. 31.726
ANTIMONY . . .	Sb	120.00	17.9	6.71	0.051	440	0.0000105	—	2.053
ARSENIC . . .	As	74.90	13.2	5.67	0.081	—	0.0000055	—	2.679
Barium . . .	Ba	136.86	36.5	3.75	0.047	1200	—	—	—
BISMUTH . . .	Bi	207.50	21.1	9.80	0.031	268	0.0000162	1.8	0.800
CADMIUM . . .	Cd	111.70	12.9	8.60	0.057	320	0.0000306	20.06	13.95
Cæsium . . .	Cs	132.70	70.6	1.88	—	26	—	—	—
Calcium . . .	Ca	39.91	25.4	1.57	0.170	red heat	—	—	—
Cerium . . .	Ce	141.00	21.0	6.68	0.045	between Sb and Ag higher than Pt	—	—	12.46
CHROMIUM . . .	Cr	52.40	7.7	6.80	(0.120)	—	—	—	—
COBALT . . .	Co	58.60	6.9	8.50	0.110	1500	0.0000123	—	9.685
COPPER . . .	Cu	63.20	7.2	8.82	0.094	1050	0.0000167	73.6	55.86
Didymium . . .	Di	145.00	22.3	6.54	0.046	—	—	—	—
Glucinum . . .	Gl	9.08	5.6	2.07	0.580	—	—	—	—
GOLD . . .	Au	196.20	10.2	19.32	0.032	1045	0.0000144	—	43.84
Indium . . .	In	113.40	15.3	7.42	0.057	176	0.0000417	53.2	—
IRIDIUM . . .	Ir	192.50	8.6	22.42	0.033	2500	0.0000070	—	—

IRON	Fe	7.2	7.86	0.110	1600	0.0000121	11.9	8.340
Lanthanum	La	22.3	6.20	0.045				
LEAD	Pb	18.1	11.37	0.031	325	0.0000292	8.5	4.818
Lithium	Li	11.9	0.59	0.941	180	—	—	10.69
MAGNESIUM	Mg	13.8	1.74	0.250	750	0.0000269	34.3	22.57
MANGANESE	Mn	6.9	8.00	0.120	1900	—	1.3	1.000
MERCURY	Hg	14.7	13.59	0.032	— 39			
Molybdenum	Mo	11.1	8.60	0.072	1600	0.0000127	—	7.374
NICKEL	Ni	6.7	8.80	0.110				
Niobium	Nb	15.0	6.27	?				
Osmium	Os	8.7	22.48	0.031	2500	0.0000065	—	6.910
PALLADIUM	Pd	9.2	11.50	0.059	1500	0.0000117	8.4	8.257
PLATINUM	Pt	194.30	21.50	0.033	1775	0.0000089	—	11.23
POTASSIUM	K	39.03	0.87	0.170	62	0.0000841		
Rhodium	Rh	104.10	12.10	0.058	2000	0.0000085		
Rubidium	Rb	56.1	1.52	0.077	38			
Ruthenium	Ru	103.50	12.26	0.061	1800	0.0000096		
SILVER	Ag	107.66	10.53	0.056	945	0.0000192	100.0	57.226
SODIUM	Na	22.99	0.97	0.290	95	0.0000710	36.5	18.30
Strontium	Sr	87.20	2.54	0.074	—	—	—	3.774
Tantalum	Ta	182.00	10.80	?				
Tellurium	Te	126.30	6.25	0.047	525	0.0000167	—	0.0004
Thallium	Tl	203.70	11.85	0.034	288	0.0000302	—	5.225
Thorium	Th	232.00	11.10	0.028				
TIN	Sn	117.40	7.29	0.056	227	0.0000223	15.2	8.237
Titanium	Ti	48.00	—	0.130?	higher than Mn			
TUNGSTEN	W	184.00	19.10	0.033				
Uranium	U	240.00	18.70	0.028				
Vanadium	V	51.10	5.50	?				
ZINC	Zn	64.90	7.15	0.094	415	0.0000291	28.1	16.92
Zirconium	Zr	90.40	4.15	0.066				

CHAPTER III.

ALLOYS.

Early Investigations. — As many valuable mechanical properties are conferred upon metals by associating them with each other, it seldom happens that metals are used in a state of purity when they are intended for industrial purposes, and this fact was discovered at a very early period of metallurgical history. The word alloy originally comes, in all probability, from the Latin *ad-ligo* (alligo), "to bind to," and not, as Sir John Pettus thought, from the Teutonic *linderen*, "to lessen," suggestive as it is of the fact that a precious metal is lessened in value by the addition of a base one.

The distinguished chemist, Dumas, eloquently pleaded, many years ago, against leaving alloys in the oblivion to which modern chemists consigned them, and there still seems to be a prevalent impression that our knowledge of the phenomena which attend the union of metals is very imperfect, and that it rests upon a slender experimental basis. We are apt to forget the extent and complexity of the subject, and Lupton* has opportunely directed attention to the number of alloys which await examination. He says:—"Hatchett recommended that a systematic examination of all possible alloys of all the metals should be undertaken. He forgot to remind any one who should attempt to follow his advice that if only one proportion of each of the thirty common metals were considered, the number of binary alloys would be 435, of ternary 4060, and of the quaternary 27,405. If four multiples of each of the 30 metals be taken, the binary compounds are 5655, ternary 247,660, and quaternary 1,013,985."

Nevertheless, if the properties of many alloys have yet to be investigated, the study of alloys generally has not been neglected. The modern bibliography relating to them is much more extensive than it is usually supposed to be, and the older writings are very full, and contain the results of far more accurate observation

* *Nature*, vol. xxxvii., Jan. 5, 1888, p. 238.

than they are credited with. In the early days of chemistry, as its history abundantly proves, alloys received much attention, and although the early chemists often failed to distinguish alloys from simple metals, or used them in unsuitable ways, they left an experimental record, the value of which is sadly unappreciated. From this record it is, incidentally, evident that the development of the art of separating metals from their ores, and from each other, was quickly followed by the acquisition of the knowledge that metals possess peculiar properties when re-united in certain proportions, and are thereby rendered more useful than they were in the pure state.

In early times some metals were used unalloyed, although at the present day they have no industrial application except in union with other metals. Antimony, for instance, now only employed as a constituent of certain alloys, was formerly cast and fashioned into ornaments, as is proved by the analyses of Virchow, and by a fragment of a very ancient Chaldean vase, which fragment, when examined by Berthelot, proved to be of pure antimony.* The implements and ornaments discovered by Schliemann abundantly show that the early Greeks were familiar with alloys of silver and gold, copper and tin, lead and silver, and with many others, all artificially prepared. Throughout the Middle Ages there seems to have been a belief that the action of metals on gold and silver was, on the whole, corrupting; and Biringuccio, in 1540, possibly seeing that this was the prevailing view, carefully defined such alloys as being "nothing but amicable associations of metals with each other"; and he further pointed out that metals must be mixed by weight, and not at random.

Views as to the Constitution of Alloys.—Passing from the sixteenth to the eighteenth century, we find four writers whose names deserve to be specially mentioned, because they seem to have been the first to indicate the direction in which modern investigation has been conducted. These are Réaumur, Gellert, Musschenbroek, and Achard, who respectively studied—1st (Réaumur), molecular change produced in a metal by heat; 2nd (Gellert), the relation of fluid metals to each other considered as solvents; 3rd (Musschenbroek), the cohesion of alloys as shown by certain mechanical properties; and 4th (Achard), the electrical behaviour of metals and alloys. It is interesting to trace the connection between the older work and the new. Réaumur,† in explaining the hardening of steel by rapid cooling from an elevated

* *Ann. de Chim. et de Phys.*, vol. xii., 1887, p. 135.

† *L'art de convertir le fer forgé en acier*, Paris, 1722, p. 321.

temperature, comes very near the modern view that a metal may, under certain conditions, pass from one allotropic state to another, for he distinctly contemplates the possibility of molecular change produced by the expulsion by heat of "sulphurs and salts" from the molecules into interstitial spaces between them. He speaks of "molecules and elementary parts of molecules," like a modern writer, and tries to show that when hot steel is rapidly cooled, "sulphurs and salts" cannot return into the molecules, but remain in the interstitial spaces; and that, therefore, the physical properties of hard steel become quite different from those of soft. If it should be urged that the analogy between carburized iron and alloys is over-strained, it may be pointed out that, in 1867, Matthiessen said, after appealing to the fact that in certain alloys the constituent metals are present in allotropic states, "I have always made a comparison between iron and steel (and alloys). This has been done to show that the carbon iron alloys behave in an analogous manner to other alloys, which cannot be looked upon as chemical combinations."*

Gellert makes the analogy of certain alloys to solutions very clear, and in his *Metallurgic Chemistry* he gives a table showing the relative solubilities of metals in each other, while in the observations which accompany it † he says, to cite one of the cases, he takes as an illustration, "Since copper and silver and copper and gold dissolve one another very readily, the copper cannot be parted from iron by means of gold or silver," probably having in mind a reaction which enables silver to be parted from gold by the action of sulphur and iron. He further clearly shows that, with regard to the solution of metals in a triple alloy, he understood the possibility of a division of a metal between two other metals acting as solvents.

The mechanical properties of alloys were investigated by Musschenbroek, who, working in the early part of the eighteenth century, made some experiments on the tensile strength of metals and alloys. He writes of "the absolute cohesion by which a body resists fracture when acted upon by force drawing according to its length," and gives the tenacity of several metals, and the alloys, brass and pewter.‡ He shows the importance of such work so clearly that it is remarkable how slowly the mechanical testing of metals developed since his time.

Achard, whose researches were published in 1784, made a very

* *Journ. Chem. Soc.*, 1867, p. 220.

† English translation of his work, London, 1776, p. 186.

‡ *Elements of Philosophy*, translated by John Colson, F.R.S., vol. i., 1744, p. 237.

extended series of experiments on multiple alloys, as well as those of simple metals. He pointed out that the relative conductivities of substances for heat and for electricity are closely related.* He devised an appliance for the experimental verification of this fact, and, as he included alloys in his researches, it may fairly be claimed that he led the way for the important generalisation that alloys may be ranged in the same order as regards their power of conducting heat and electricity, which was made by Wiedemann and Franz in 1853-9.

The necessity of metals being pure when added to each other was hardly recognised until the eighteenth century, and Duhamel, who contributed the article on alloys to the *Encyclopédie Méthodique* in 1792, appears to have been the first writer to insist on the necessity for making exact experiments upon alloys with metals which possess a high degree of purity and on effecting their union by heat in closed vessels. He further pointed out that up to his time no chemist had taken these precautions, and it is certain that in conducting some modern experiments they have been neglected.

In the early part of the nineteenth century researches on alloys became more numerous; they were mainly directed to ascertaining the effect on the density of metals produced by alloying them and to determining the effects of slow cooling on alloys with low melting points. Of such a nature was the work of Ermann in 1827 and of Rudberg (1830-1). Ermann called attention to the peculiar behaviour of alloys of lead and tin when solid. Rudberg studied anomalies in these alloys when in the liquid state.

Regnault showed that the specific heats of certain fusible alloys were greater near 100° than the mean specific heat of their constituents, and this fact appears, as Spring has shown,† to have induced Person to undertake researches on the latent heat of alloys and on these specific heats.

Undoubtedly one of the greatest works on alloys of the present century was that of Matthiessen, who studied the electrical resistance of metals and alloys, and was led to the conclusion that in many cases metals are present as allotropic modifications—that is, in totally different forms from those in which we ordinarily know them.

It is by no means easy to investigate the molecular constitution of alloys, but evidence may be gathered in the following ways:

* *Sammlung physikalischer und chemischer Abhandlungen*, Berlin, 1784, vol. i.

† *Bull. de l'Académie Royale de Belgique*, 1886 (3), vol. xi. p. 355.

1. By comparing the properties of an alloy with those of its constituent metals.

2. By studying the behaviour of alloys in passing from the liquid to the solid state, and conversely in passing from the solid to the liquid.

3. By determining the physical constants of solid alloys, such as the melting point, specific gravity, specific heat, electrical resistance, electromotive force, and their mechanical properties, such as tenacity and extensibility.

First we must consider the methods of producing alloys, for the union of metals may be effected in three ways:

1. By fusion—that is, by causing metals to unite by melting them together.

2. By compression of the powders of the constituent metals.

3. By electro-deposition.

Union of Metals by Fusion.—The first method, by fusion, is, of course, the method ordinarily adopted. One of the metals is melted, and the other is added to it, sometimes in the fluid state, but often in the solid. The product—the alloy—will have very different properties from those possessed by either of the constituent metals. Every metal has, of course, a definite melting point, but, apart from the heat initially required to melt a metal, we find that the union of metals is sometimes attended with an evolution and sometimes with an absorption of heat.

The following metals evolve heat when they are united:—aluminium and copper, platinum and tin, arsenic and antimony, bismuth and lead, gold and just-melted tin; while on the other hand, lead and tin when united absorb heat, that is produce cold when their union takes place. There are many other cases.

In the case of many metals these effects can only be demonstrated by the aid of delicate instruments. There is, however, a simple case in which the union of metals is attended with a considerable diminution of temperature; it is an experiment we owe to Mohr, and it will be shown subsequently that its explanation is a very complicated one. Take tin, lead, and bismuth in equivalent proportions, as finely divided as possible and mix them with eight equivalents of mercury as rapidly as may be, under conditions in which heat is not transmitted to the mixture from the walls of the containing vessel, and it will be found that the temperature falls from the ordinary temperature of the room + 17° C. to - 10° C., so that if a vessel containing water be placed in the mixture the water will be frozen. The experiment proves that by the union of metals, using mercury as a solvent, a freezing mixture may be produced.

Union of Metals by Compression.—Now turn to the second method by which metals may be caused to unite, that is, by compressing strongly the powders of the constituent metals. Since 1878, the labours of Prof. Walthère Spring, of the University of Liège, have been mainly devoted to the study of the effect of compression on various bodies.*

The particles of a metallic powder left to itself at the ordinary atmospheric pressure will not unite, but by augmenting the points of contact in a powder, the result may be very different. Spring's experiments were made with the aid of a compression apparatus, the general form of the appliance employed being shown in the diagram, Fig. 23. The metallic powder is placed under a short

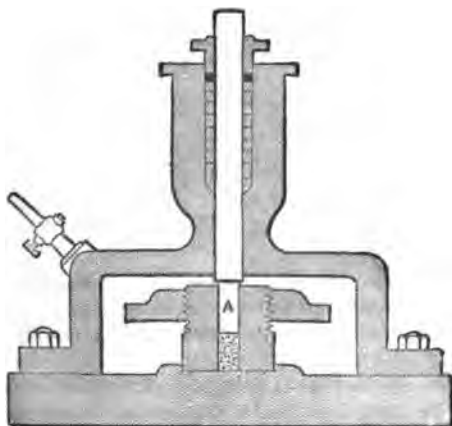


FIG. 23.

cylinder of steel, A, in a cavity in a steel block divided vertically, held together by a collar, and placed in a chamber of gun metal, which may be rendered vacuous. The pressure is applied to a cylindrical rod passing through the stuffing box. Under a pressure of 2000 atmospheres on the piston, or 13 tons on the square inch, lead, in the form of filings, becomes compressed into a solid block, in which it is impossible to detect the slightest vestige of the original grains, while under a pressure of 5000 atmospheres lead

* *Bull. de l'Académie Royale de Belgique* (2), vol. xlv. (1878), No. 6; (2), vol. xlix. (1880), No. 5. See also subsequent papers in the same publication; in the *Bull. Soc. Chim.*, Paris, and in the *Berichte der Deutsch. Chem. Gesellschaft* (Bildung von Legirungen durch Druck), vol. xv. p. 595.

no longer resists the pressure, but flows, as if it were liquid, through all the cracks of the apparatus, and the piston of the compressor descends to the base of the cylindrical hole, driving the lead before it. The more interesting results were obtained by Spring with crystalline metals. Bismuth, as is well known, is crystalline and brittle, yet fine powder of bismuth unites, under a pressure of 6000 atmospheres into a block very similar to that obtained by fusion, having a crystalline fracture. Tin, when compressed in powder unites, and if it is made to flow through a hole in the base of the compression apparatus, the wire so formed sometimes, though not always, emits the peculiar "cry" of tin when bent. The following table shows the amount of pressure required to unite the powders of the respective metals:—

					Tons Per Square Inch.
Lead	unites at	.	.	.	13
Tin	"	.	.	.	19
Zinc	"	.	.	.	38
Antimony . .	"	.	.	.	38
Aluminium .	"	.	.	.	38
Bismuth . . .	"	.	.	.	38
Copper	"	.	.	.	33
Lead	flows at	.	.	.	33
Tin	"	.	.	.	47

We know that combinations are produced when certain bodies in solution are submitted to each other's action. But do solids combine? Is the alchemical aphorism "That bodies do not react unless they are in solution" true? Experiment proves that such solution is not necessary. Take, for example, two anhydrous salts—iodide of potassium and corrosive sublimate, both in a dry condition. When they are mixed in a mortar they unite, as is shown by the vermilion-coloured iodide of mercury which is produced. But do solid metals combine, in the sense in which chemical combination is possible between metals, when submitted to each other's action under the conditions which prevail when their powders are compressed? Mohr has pointed out* that cohesion is a form of chemical affinity, and the experiment cited, of freezing water by the cold produced by amalgamation, affords valuable evidence in support of his view. It occurred to M. Spring that if there be true union between the particles of a metallic powder when submitted to great pressure in the appliance shown in Fig. 23, it ought to be possible to build up alloys by compressing the powders of the constituent metals, and he urged that the

* *Liebig's Ann.*, vol. cxcvi. (1879), p. 183.

formation of alloys by pressure would afford the most conclusive proof that there is a true union between the particles of metals in the cold, when they are brought into intimate contact. Experiment proved that this reasoning is correct, for by compressing in a finely divided state, fifteen parts of bismuth, eight parts of lead, four parts of tin, and three parts of cadmium, an alloy is produced which fuses at 100°C . It is necessary, however, to compress the mixed powder twice, crushing and filing up the block obtained by the first compression because the mechanical mixture of the constituent metals is not sufficiently intimate to enable a uniform alloy to be obtained by a single compression. The alloy produced fuses in boiling water, actually at 98°C ., although the melting point of the most fusible of its constituents, the tin, is 282°C . It may be urged that by compressing these powders heat is evolved, and that this heat may be sufficient to produce incipient fusion of the metallic powders, or at all events, may exert a material influence on the result obtained. This objection has been experimentally anticipated by Professor Spring. First the compression is effected with extreme slowness, and therefore there can be no question as to the sudden evolution of heat, as would be the case if the powders were compressed by impact instead of by slow squeeze; and, to sum the matter up briefly, Spring calculates an extreme case—that if it be granted that all the work done in compressing the powders were actually translated into heat, it would only serve to heat a cylinder of iron 10 mm. in height, and 8 mm. in diameter (the dimensions of cylinder A, Fig. 23, used in his apparatus), 40.64°C .

In order that direct experimental evidence might not be wanting Spring took the organic body, phorone, a hard, crystalline substance which melts at 28°C ., and compressed it exactly as in the case of the metallic powders.* He took the precaution to place a shot of lead on the top of the powder before submitting it to compression. Only imperfect union of the particles of phorone resulted. The conclusion of the experiment proved that the shot remained where it had been placed at the top of the column, and, therefore, the 28° necessary to melt the substance had not been evolved, for if it had the shot must have fallen through the fluid mass. It is, then, absolutely safe to conclude that, in the compression of bismuth, for instance, there can be no question of the evolution of the heat necessary for the fusion of the metal.

It appears to be also quite safe to conclude that it is proven that *solid* metals possess the power of reacting on each other

* *Bull. Soc. Chim.*, vol. xli. (1884), p. 488.

and forming alloys, provided their particles are really in contact.

Union of Metals by Electro-Deposition.—The formation of alloys by the electrolytic deposition of the constituent metals is a subject of great importance, and although the union of metals is usually effected by fusion, fire is not the only agent which can be employed for this purpose. Two or more metals can be deposited side by side by the aid of the electric battery. No statistics as to the amount of precious metals annually employed for electro-deposition in Birmingham, the early home of electro-metallurgy, are available, but it is known that a single works in Paris, belonging to M. Christofle, deposits annually six tons of silver, and it has been estimated that the layer of silver of the thickness actually deposited on various articles would, if spread out continuously, cover an area of 140 acres. Copper and zinc may be deposited by electrolysis so as to form brass, and all the beautiful bronzes and alloys of the Japanese can be obtained by galvanic agency; and, further, by suitable admixture of gold, silver, and copper, red gold, rose-coloured gold, or green gold may be deposited, so that the electro-metallurgist has at his command the varied palette of the decorative artist.

Liquation.—It is now necessary to examine more closely the mutual relations of the metals when united. Metals may be mixed in the fused state, but it by no means follows that they will remain in admixture if they are allowed to cool slowly, or sometimes even rapidly. In fact, a cooling mass of mixed metals often behaves much as water containing suspended matter does in freezing, when the ice first formed rejects the foreign matter, and as has been shown by the classical researches of Levol,* the portion of the alloy which first solidifies rejects certain other portions of the constituent metals. This action is called liquation. The term is also applied in a somewhat wider sense to the actual isolation of the components of ores or of alloys from each other. For instance, when an ore or mixture of metals is exposed to a degree of heat sufficient only to melt the most fusible member or constituent present in the mass, it flows away from the unmelted residue. In the case of alloys the importance of liquation has been fully recognised. If lead and zinc be thoroughly mixed in the fused state, and slowly cooled in a deep mould, the separation will be almost complete, and it will also be seen that it is easy to break off one corner at the side where the zinc has separated itself, and to flatten out another one, which shows it to be nearly

* *Ann. de Chim. et de Phys.*, vol. xxxvi. (1852), p. 193; vol. xxxix. (1853), p. 163.

pure lead. Take again the case of what was a triple admixture of lead, antimony, and copper, thoroughly mixed when fluid, and cooled in a cylindrical mould. The copper and the antimony unite, but they reject much of the lead, and drive it to the centre of the mass, so that the solidified cylinder, when broken across, presents a ring of the purple copper-antimony alloy surrounding a malleable core. Silver and copper alloys behave in a similar manner, but in any mixture of fused silver and copper, one particular alloy of these metals is formed which is driven outward or inward in the cooling mass according to whether silver or copper is in excess in the bath. In all these cases the separation is never complete; the lead retains some 1.6 per cent. of zinc, and the zinc about 1.2 per cent. of lead. The copper and antimony retain a small amount of lead, and the lead a small amount of copper and antimony, as is shown by some very careful experiments of Dr. E. J. Ball, to which reference has already been made. The solid mass in all these cases is a mixture of solidified solutions of the metals in each other.

Dr. Guthrie investigated this side of the problem at some length.* It is difficult to give a brief account of his work, but his conclusions may be stated as follows: He considers that certain alloys in cooling behave as a cooling mass of granite would; clear molten granite would throw off, in cooling, "atomically definite" bodies, leaving behind a fluid mass, which is not definite in composition, as the quartz and the felspar undergo solidification before the mica. In alloys much the same thing happens, for where a molten mass of lead and bismuth or bismuth and tin cools, a certain alloy of the metals falls out, just as the quartz and felspar did, and ultimately the most fusible alloy of the series is left, which Dr. Guthrie calls the eutectic alloy. It is the most fusible alloy of the series, but the proportion between the constituent metals are not atomic proportions, and Guthrie says that "the pre-conceived notion that the alloy of minimum temperature of fusion must have its constituents in simple atomic proportions, that it must be a chemical compound, seems to have misled previous investigators;" but he adds "that certain metals may, and do unite with one another in the small multiples of their combining weight may be conceded; the constitution of eutectic alloys is not in the ratio of any simple multiple of their chemical equivalents, but their composition is not on that account less fixed, nor are their properties the less definite."

Guthrie dealt only with alloys of low melting points, such as

* *Phil. Mag.*, vol. xvii. (1884), p. 462.

the fusible metals, and it remains to be seen whether the observation will apply to alloys with higher melting points. It does apply, at least, to the silver-copper alloys, which melt below 940°C . For further information upon this point we must wait for the development of Mendeléef's theory of solution. He regards solutions as strictly definite, atomic, chemical combinations at temperatures higher than their dissociation temperatures. Definite chemical substances may be either formed or decomposed at temperatures which are higher than those at which dissociation commences; the same phenomenon occurs in solution; at ordinary temperatures they can either be formed or decomposed.

Liquation is very marked in the case of copper-silver alloys, and it is well known in Mints that when molten alloys of certain metals are cooled, groups of the constituent metals, or even the constituent metals themselves, separate, and thus occasion irregularity in the composition of the solidified mass. The phenomenon has been carefully studied by, amongst others, Lazarus Ercker, and Jars, whilst in more modern times the researches of D'Arcet in 1824, of Mercklein in 1834, of Levol in 1854, have shown that ingots of silver and copper are not homogeneous throughout. Levol cast the alloy to be examined either in a cubical iron mould of 45 mm. side, or in a sphere 50 mm. in diameter. He concluded that the only homogeneous copper-silver alloy was that containing 71.89 per cent. of silver, and he considered this to be a

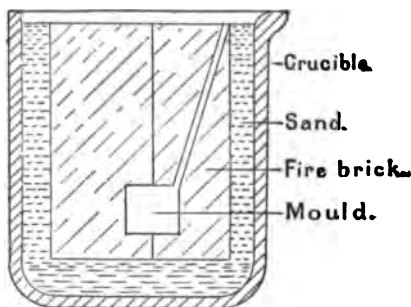


FIG. 24.

definite combination of the two metals, with the formula Ag_3Cu_2 (or Ag_3Cu_2 if 63.34 be taken as the atomic weight of copper). All other alloys of silver and copper he viewed as mixtures of this definite alloy with excess of either of the metals. In 1875 the author*

* *Proc. Roy. Soc.*, vol. xxiii. (1875), p. 481.

repeated many of Levol's experiments, and gave evidence for modifying his view that the only homogeneous alloy of silver and copper is that which contains 71.89 per cent. of silver. The uniformity in composition of the series of copper-silver alloys depends greatly on the method of cooling. By slow cooling many alloys, other than the one mentioned above, may be made as uniform as it, its peculiarity consisting in the fact that its composition is uniform whether it is cooled slowly or rapidly. In order to ascertain whether liquation is modified if the cooling be greatly protracted, cubical moulds, about 4 to 5 millimetres in side, of firebrick (Fig. 24) were employed. These could easily be heated to bright redness, and slowly and uniformly cooled. The following results show that the maximum difference in the composition of an alloy containing 925 parts of silver and 75 parts of copper was only 1.40 per thousand when the alloy was slowly cooled, while it was as much as 13 parts per thousand when the alloy was rapidly cooled :

Vertical Plane	a.	925.7	Horizontal Plane	1.	924.8
	b.	925.0		2.	925.0
	c.	925.0		3.	924.9
	d.	925.0		4.	924.9
	e.	925.4		5.	925.0
	f.	924.3		6.	925.1
	g.	925.0		7.	925.1
	h.	925.3		8.	925.1
	i.	925.3		9.	925.0
	j.	925.3		10.	925.0
	k.	924.3	Corners	α.	924.1
	l.	925.3		β.	924.1
	m.	925.3		γ.	924.1
	n.	924.4		δ.	924.4
	o.	925.0		ε.	924.0
	p.	924.3		ζ.	924.2
	q.	925.0		η.	924.2
	r.	925.3		θ.	923.9
	s.	925.0	"Dip assay," 924.9. Maximum difference [between the centre and the corners], 1.40 per thousand.		
	t.	924.9			
	u.	924.3			
	v.	924.7			
	w.	924.9			
	x.	924.9			
	y.	925.3			

The diagram (Fig. 25) shows the position in the cube corresponding to the letters and figures given above.

Levol also showed that in solidifying alloys of lead with the precious metals, if the latter are present in small quantity, they are driven towards the centre of the solidifying mass. Gowland

and Koga* have shown that when 984.37 parts of silver and 14.80 parts of bismuth are melted and cast into an open ingot mould so as to give an ingot weighing about 1000 troy oz., the portions of the ingot which remain longest fluid are richer in silver than the others. The entire question has recently been reviewed by Peligot,† who has endeavoured to ascertain, by assaying various parts of an ingot of gold weighing 13 lbs., whether he could detect the effects of liquation. The ingot contained 900 parts of gold in 1000, the alloying metal being principally copper, and he concluded that, within the limits of the errors of observation, there was no evidence of liquation. As this is a question of much industrial importance in relation

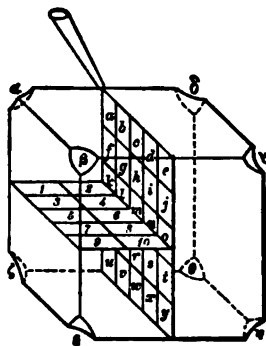


FIG. 25.

to the precious metals, the author has made further investigations into this subject, and in view of the difficulty of obtaining more precise evidence on the point the following experiment was made: A gold ingot of a fineness of 984.7, the alloying metal being silver, was melted and poured into a spherical mould of iron. The temperature of the molten metal was much higher than that of the mould, and probably in this case the position of the metal which solidified last would be situated somewhere above the geometrical centre of the mass. From the sphere of solid gold, which was 3 inches in diameter and weighed 140 oz., a disc, $\frac{3}{8}$ inch in thickness, and of the full diameter of the sphere, was cut in a vertical plane. This disc, which weighed 31 oz., was rolled in two directions at right angles to each other to a convenient thickness for cutting with shears, and assay pieces were cut from points distributed over its entire surface. The results of eighty-two assays afforded no clear evidence of systematic rearrangement, for although there appeared to be an enrichment towards the upper part to the extent of $\frac{1}{100000}$ ths, such small differences as existed in the assays made on metal taken from the same horizontal planes could not be regarded as being due to any definite redistribution of the metal. It will thus be evident that gold of high standard does not, like silver, show any marked tendency to reject on solidification the baser metal with which it is

* *Journ. Chem. Soc.*, vol. II. (1887), p. 410.

† *Bull. Soc. d'Encouragement*, vol. IV. (1889), p. 171.

associated. It is well known, however, that there is a development of crystallisation, and that other remarkable changes are produced in the structure of pure gold by the addition of minute quantities of lead, bismuth, and certain other metals. As yet, there can be said to be no sufficient evidence to show that gold, alloyed with silver and copper and properly mixed in the molten state, is not practically homogeneous when solid.

On the other hand, Mr. E. Matthey* has recently shown that by casting an alloy of gold and platinum containing 900 parts of gold and 100 parts of platinum, in the identical mould above described, there is a concentration of platinum towards the centre of the mass, the gold and platinum being as 900 gold to 98 platinum on the exterior, against 845 gold and 146 platinum at the centre of the mass. Consequently, it is evident that gold on solidifying does tend to free itself from associated platinum, though no effect of the kind can be detected by careful assay in the case of associated copper or silver.

It is, however, in relation to the metallurgy of iron and steel that the question of liquation is of primary importance. There can be no doubt that when an ingot of steel slowly cools, phosphorus, sulphur, and carbon, and, to a less degree, manganese and silicon, tend to separate from the mass and to become concentrated in that portion of the ingot which solidified last. Of the earlier researches on this subject, probably the most important is that of Snelus.† He cut an ordinary steel ingot into slices parallel to the base, and analysed borings taken from each slice along a diagonal line from one corner to the centre, and numbered from 1 to 6, passing from the bottom left hand corner to the centre. His results are given in the following table, and show that, although the bottom layer is uniform, the carbon, sulphur and phosphorus are driven towards the centre of the mass:—

	Top.			Bottom.		
	Carbon.	Sulphur.	Phosphorus.	Carbon.	Sulphur.	Phosphorus.
1	0.44	0.032	0.041	0.44	0.048	0.060
2	0.54	0.048	0.060	0.42	0.056	0.062
3	0.57	0.080	0.086	0.41	0.048	0.054
4	0.61	0.096	0.097	0.40	0.048	0.054
5	0.68	0.120	0.111	0.38	0.048	0.058
6	0.77	0.187	0.142	0.37	0.044	0.052

* *Phil. Trans.* [A] vol. clxxxiii. (1892), p. 629; *Proc. Roy. Soc.*, vol. xlvii. (1890), p. 180.

† *Journ. Iron and Steel Inst.*, 1881, p. 379.

There can be no doubt, therefore, that constituents whose presence is injurious to the mechanical properties of steel, find their way towards the top of the ingot. In steel ingots destined for the manufacture of guns, it is usual to cut off the tops, which are unsound as well as impure. The importance of this procedure has been widely recognised.* It is clear that the action of liquation cannot be neglected in making large castings and forgings, and probably gives rise to fractures that have hitherto been regarded as mysterious.

In the case of pig iron it is possible to isolate products of liquation, as has been shown by M. Lencauchez,† who heated fragments of iron to a temperature of 940° for 100 hours. At the end of this time a number of spherical grains sweated out from the surface of the fragments. Analysis of these exudations showed that they contained from 4 to 6 per cent. of phosphorus, from 0.6 to 0.8 per cent. of silicon, from a trace to 1.5 per cent. of graphite carbon, and from 0 to 1.24 per cent. of combined carbon. The original pig iron contained about 3.5 per cent. of total carbon, 2.6 of silicon, and 1.9 of phosphorus. The composition of these exudations, therefore, is that of pig iron impoverished in carbon and silicon, but considerably enriched in phosphorus.

If lead, tin, and zinc are melted together, and left at rest in a fused condition, no separation takes place if the proportion of tin exceeds a certain amount; but if the quantity of tin is less than this, the alloy separates into two layers, each layer consisting of a ternary alloy of the three metals. Dr. C. R. A. Wright and Mr. C. Thompson‡ have examined the nature of this separation, and the composition of the alloys under different conditions. The heavier alloy, they found, consists of a saturated solution of zinc in lead containing tin, whilst the lighter consists of lead in zinc containing tin. The two alloys always correspond with two conjugate points on the solubility curves of zinc in lead-tin, and of lead in zinc-tin. The tin is not distributed equally in the two alloys, except when present in a particular proportion, which varies with the ratio of zinc to lead. With less tin than this, the lighter alloy takes up the excess of tin; with more, the heavier takes up the excess.

* Maitland, *Min. Proc. Inst. C.E.*, vol. lxxxix. (1887), p. 127. See also Eccles, *Journ. Iron and Steel Inst.*, No. 1 (1888), p. 70, and the discussion on Greenwood's paper on the "Treatment of Steel by Hydraulic Pressure," *Min. Proc. Inst. C.E.*, vol. xcvi., 1889.

† *Mém. Soc. Ing. Civile*, 1887.

‡ *Proc. Roy. Soc.*, vol. xlv. (1889), p. 461.

Solution of Metals in Metals.—Much progress has recently been made in these researches, and the author is indebted to his friend Dr. Alder Wright, F.R.S., who has prepared for this book the following account, not only of his recently published* researches on alloys, but of work still in progress.

He states that in the course of a series of experiments lasting over several years and not yet fully completed, the following results have been arrived at.

Of the 36 pairs which it is possible to form with the 9 metals Pb, Bi, Al, Zn, Sn, Ag, Sb, Cd, Cu, the great majority have been found to possess the property of *completely blending with one another so as to form a homogeneous fluid* stable for many hours when they are heated to such a temperature that the whole mass remains liquid. On cooling, segregation occurs in many cases during solidification. Five pairs, however, are exceptional when the components lie within the undermentioned limits; when well intermixed by stirring and then allowed to stand molten for some hours at an equable temperature (preferably by pouring the fluid mass into clay test-tubes heated to the required temperatures in a bath of molten lead), two alloys separate from one another; the denser consists mainly of the heavier metal, A, containing in solution a small quantity of the lighter metal, B, the amount dissolved increasing with the temperature; whilst the lighter alloy consists, conversely, mainly of B, with a little A. Using the nomenclature proposed by Sir G. G. Stokes, these pairs of metals form *real* alloys only when employed outside of the limits stated, while within these limits they form *ideal* alloys only.

It must be remembered that the word *ideal* is used in the sense of imaginary or *unreal*, as the alloys probably do not actually exist; they give rise to mixtures that are incapable of permanently remaining homogeneous, being analogous to intimate emulsions of oil and water, or ether and water, rather than to true mutual solutions of alcohol and water. The term "stable" and "unstable" alloys may also be conveniently used to distinguish the two classes respectively.

I. Mean Values of Limits for Lead and Zinc (Average of Numerous Determinations).

At about 650° C	.	Between	{ Pb = 98.76 Zn = 1.24	and	{ Pb = 1.14 Zn = 98.86
" 800° C	.	"	{ Pb = 98.70 Zn = 1.30	"	{ Pb = 1.57 Zn = 98.43

* Proc. Roy. Soc., 1889-1893.

II. *Bismuth and Zinc.*

At about 650° C	.	Between	{ Bi = 85.72 Zn = 14.28	and	{ Bi = 2.32 Zn = 97.68
" 750° C	.	"	{ Bi = 84.82 Zn = 15.18	"	{ Bi = 2.47 Zn = 97.53
" 800° C	.	"	{ Bi = 84.17 Zn = 15.83	"	{ Bi = 2.52 Zn = 97.48

III. *Lead and Aluminium.*

At about 800° C	.	Between	{ Pb = 99.93 Al = 0.07	and	{ Pb = 1.91 Al = 98.09
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IV. *Bismuth and Aluminium.*

At about 800° C	.	Between	{ Bi = 99.72 Al = 0.28	and	{ Bi = 2.02 Al = 97.98
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V. *Cadmium and Aluminium.*

At about 750° C	.	Between	{ Cd = 99.78 Al = 0.22	and	{ Cd = 3.39 Al = 96.61
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(According to the text-books, Aluminium mixes freely with both Bismuth and Cadmium.)

Out of the above-mentioned 9 metals, 84 different combinations can be formed taking them 3 at a time. Of these, 55 combinations invariably form *real* alloys when heated so that the whole mass remains liquid; whilst 29 give rise to *ideal* ternary alloys when the proportions in which the materials are used lie within certain limits. These limits are delineated graphically by a method due to Sir G. G. Stokes (see p. 78). A triangle (preferably equilateral) is drawn, at the three corners of which weights are supposed to be placed in the ratio of the relative quantities of the 3 metals respectively present in a given mixture of them; then this mixture is denoted by a point within the triangle representing the centre of gravity of the 3 weights of the metals. An *ideal* alloy gives rise to two "conjugate points," representing the heavier and lighter alloys respectively into which the mass divides itself; the line joining the points is referred to as a "tie-line" or "tie." With a sufficiently extended series of observations at a constant temperature, T° , with the metals in suitably varying proportions, the various pairs of conjugate points deduced, map out an area inside the triangle corresponding with the limits of composition within which *ideal* alloys result, and outside of which *real* alloys are formed at the temperature T° . The loci of the two series of points represent curves, conveniently

designated "critical curves," indicating the boundary of this limiting area.

The 29 possible kinds of ideal ternary alloys above mentioned are divisible into two classes characterised by entirely different kinds of critical curves, and differently shaped areas enclosed by them.

In the first class (23 in number), calling the 3 metals respectively A, B, and C, 3 pairs can be taken, respectively AB, AC, and BC. Of these, one pair, AB, is "immiscible"—i.e., is one of the 5 binary combinations furnishing ideal alloys when mixed within the limits above stated; or, in other words, A will mix in all proportions with C, as also will B with C; but A will not mix in all proportions with B. The third metal, C, which will mix in all proportions with either A or B, is conveniently designated the "solvent" metal. The 23 combinations of this kind are—

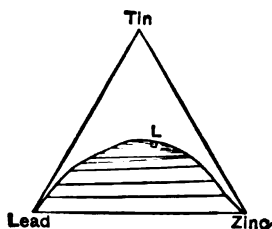
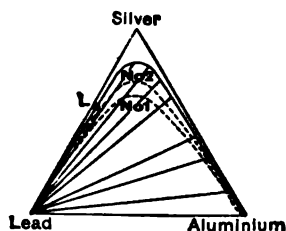
A.		B.	C = "Solvent."
Pb	...	Zn	} either Sn, Ag, Sb, Cu, or Cd = 10
Bi	...	Zn	
Pb	...	Al	} either Sn, Ag, Sb, or Cu = 8
Bi	...	Al	
Cd	...	Al	either Sn, Ag, Sb, Cu, or Zn = 5
			23

The critical curves deduced at certain definite temperatures for the majority of these combinations have been recorded in various papers communicated to the Royal Society, whilst the determination of the remainder is in progress. In all cases, when the triangular delineation is effected with the immiscible metals A and B at the base, and the solvent metal, C, at the apex of the triangle, the two series of points respectively representing the heavier and lighter conjugate alloys formed in a series of experiments with gradually increasing proportions of solvent metal form two branches or portions of a single curve, rising upwards from the base line to a maximum elevation, and then descending again to the base; so that the area enclosed by the critical curve is roughly a segment of an ellipse. The point where the two branches meet and merge into one another (or point where the system of tie-lines dwindles down to a point and vanishes) is conveniently designated the "limiting point." As a rule this is not the highest point of the curve, but lies on one side or the other, nearer to the base.

Thus in the annexed diagrams, Fig. 25a, L represents the limiting point, lying to the *right* of the highest point of the curve in

the case of lead-tin-zinc alloys, and to the *left* in that of lead-silver-aluminium alloys, Fig. 25*b*.

With certain combinations of metals, peculiarities are traceable either as regards the contour of the critical curve, or the direction in which the tie-lines slope, &c., which lead to the conclusion that definite atomic compounds are formed of the solvent, C, with one or other of the other metals, A or B; thus with alloys containing simultaneously zinc and silver, two compounds (respectively AgZn_2 and Ag_2Zn_3) are thus suggested by bulges (inwards or outwards) of the critical curve; similarly with mixtures containing bismuth and antimony, the existence of the compound Bi_2Sb_3 is suggested in the same kind of way. In the case of alloys containing tin and lead (and in these only) the lower tie-lines slope in one direction, and the upper ones in the opposite, as indicated in the figure for alloys of Pb, Sn, Zn; a result

FIG. 25*a*.FIG. 25*b*.

apparently due to the formation of the compound SnPb_2 . Again, with alloys containing lead and cadmium, a number of ties all converge together to nearly the same point, indicating the existence of the compound CdPb_2 ; whilst similar indications suggest the existence of the compound, SnZn_2 .

As regards the two immiscible metals, it is noteworthy that the relative proportion in which they are present at the limiting point is not at all constant, but varies within pretty wide limits according to the nature of the solvent metal.

For the same temperature, and all other things being the same, the substitution of *aluminium* for *zinc* as lighter immiscible metal appears always to *raise* the critical curve—i.e., the limits with zinc as lighter metal lie *inside* the corresponding limits with aluminium. Thus the dotted line, No. 2, Fig. 25*b*, representing Pb, Ag, Al alloys, shows the corresponding curve obtained

with Pb, Ag, Zn alloys, omitting bulges. A similar result is noticeable as regards *lead* and *bismuth*, the critical curve with bismuth as heavier immiscible metal always lying *inside* that similarly deduced with lead. On comparing curves obtained with the same immiscible pair at about the same temperature with the solvents *cadmium*, *silver*, *tin*, and *antimony* respectively, it is found that the cadmium and silver curves lie *outside* the tin curve, which again lies outside the antimony curve. Thus the dotted line, No. 1, in the figure representing Pb, Ag, Al alloys indicates the corresponding curve obtained with Pb, Sn, all alloys, lying well inside the continuous curve.

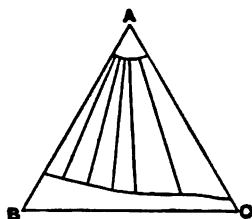


FIG. 25c.

The second class of ternary alloys above referred to contains six members :—

A.		B.		C.
Zn	...	Bi	...	Pb
Al	...	Bi	...	Pb
Bi	...	Al	...	Zn
Pb	...	Al	...	Zn
Al	...	Bi	...	Cd
Al	...	Pb	...	Cd

the characteristic of this class being that *two* of the three pairs (AB and AC) are "immiscibles," whilst the third pair (BC) consists of metals miscible in all proportions.

When the results of suitable series of observations are plotted with the metal A at the apex of the triangle, and B and C at the ends of the base, the two series of conjugate points trace out *two separate curves* that do not run into one another at a limiting point; one of these curves cuts off a 3-sided figure at the apex of the triangle bounded by the upper parts of the sides and this upper critical curve; the other similarly cuts off a 4-sided figure at the base, bounded by the base, the lower portions of the sides, and this lower critical curve: the area within which all points

denote *ideal* alloys only is consequently a 4-sided figure bounded by the middle portions of the sides of the triangle, and the upper and lower critical curves, as indicated in the figure. These 6 pairs of critical curves are under investigation.

The set of 9 metals above mentioned does not enable a ternary mixture of members of the set to be made in which *all three* of the pairs AB, AC, BC, are immiscibles. But there does not appear to be any reason *a priori* why such a mixture should be incapable of existence; when in suitable proportions it should divide into three layers—*viz.*, chiefly A with a little B and C; principally B with a little A and C; and mainly C with a little A and B. Analogous mixtures of non-metallic fluids can exist; thus a mixture of *petroleum hydro-carbon* (burning oil), *castor oil* (not greatly adulterated with other oils), and *water* separates into three distinct layers when shaken up and allowed to stand.

No less than 126 quaternary combinations can be formed out of the 9 metals above mentioned. Of these, 55 always form real alloys, whilst 71 give rise to ideal alloys when mixed in proportions inside certain limits. These limits may be delineated by supposing the 4 constituents to be placed at the 4 solid angles of a tetrahedron (preferably regular), when the centre of gravity of the whole is a point indicating the particular mixture used. The conjugate points furnished by a suitable series of ideal alloys map out a "critical surface" inside the tetrahedron.

Since 6 pairs can be formed from the 4 constituents (AB, AC, AD, BC, BD, CD) 6 classes of quaternary ideal alloys can theoretically exist according as 1, 2, or more of these 6 pairs are "immiscibles." Members of some of these classes are now under investigation.

126 quinary, 84 sexenary, 36 septenary, and 9 octenary combinations can also be formed from the above 9 metals; making (with those above mentioned and the mixture of the whole 9) 502 different alloys in all. Of these, real alloys (no matter in what proportions the constituents are mixed) are afforded by only 31 quinary, 9 sexenary, and 1 septenary combinations, all the others furnishing ideal alloys when mixed in proportions not outside of certain limits. In all, 320 combinations out of the 502 possible ones can thus yield ideal alloys, whilst the other 182 combinations yield real alloys no matter in what proportions they are mixed.

The experiments to which Dr. Alder Wright has devoted so much time and care afford another illustration of the similarity in the behaviour of molten alloys and ordinary solutions of salts, a similarity that is becoming more evident every day.

Action of Electric Currents on Molten Alloys.—In fur-

ther tracing the analogies between alloys and saline solutions, it will be well to see what takes place when a current of electricity is passed through an alloy. Take first the case of a fluid alloy through which a current is passed. We have spoken of alloys as solutions; if they be ordinary chemical solutions it has been urged that an electric current of sufficient strength ought to decompose them, and it becomes a most important question to determine whether an ordinary metallic alloy can conduct electrolytically like a salt solution, or whether it conducts, as a metal would, that is, without being decomposed.

The question therefore arises, can a well-marked alloy, or a quasi-compound, be in the slightest degree electrolysed by an exceedingly intense electric current? Some experiments conducted by M. Gérardin,* in 1861, satisfied him that amalgams of sodium and mercury might be decomposed by an electric current, with partial separation of the constituent metals. The experiments were repeated by Dr. Obach† who employed the apparatus shown in the diagram (Fig. 26). The sodium amalgam is enclosed in the two

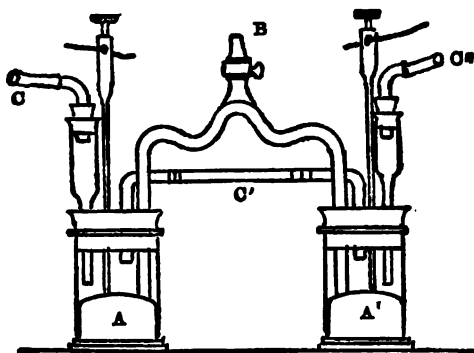


FIG. 26.

glass vessels, A A', and metallic communication between them is effected by opening the stop-cock, B, and sucking the amalgam into the bent tube. An atmosphere of dry hydrogen is provided, by the tubes, C C' C'', and the current is transmitted through the amalgam by the battery terminals shown. Subsequent examination of the sodium amalgam proved that no separation had been effected. The composition of the amalgam was unaltered by the

* *Comptes Rendus*, vol. liii. (1861), p. 727.

† *Poggendorff's Ann. der Phys. u. Chemie*, sup. vol. vii. (1876), p. 280.

passage of the current. He also used a W-shaped tube containing melted alloys, and proved that no decomposition could be observed after the passage of the current.

In 1887, at the request of the Electrolysis Committee of the British Association, the author took up the inquiry* and by employing an intense electric current from secondary cells, showed that no separation took place either in certain alloys of lead and gold, or in alloys of lead and silver, even with so strong a current as 300 ampères. The method employed is indicated by the diagram (Fig. 27). The alloy, C D, under examination was placed in cavities cut in a fire-brick, shown at E, and the cables from a secondary battery were connected by means of copper holders with wrought-iron terminals, A B. The experiments are given in detail in the Report of the British Association for 1887, and it will be sufficient to say here that as the question at present stands, it would seem that fluid alloys conduct just like metals, and not like salt solutions; but, as Dr. Lodge has pointed out with reference to these experiments, "if the question as to the possibility of the electrolytic separation of true alloys of metals should be answered in the negative, there must surely remain a group of bodies on the borderland between alloys proper and electrolytes, among which some gradual change from wholly metallic to wholly electrolytic conduction is to be looked for."

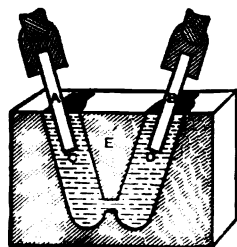


FIG. 27.

Conduction of Electricity by Alloys at High Temperatures.

—It has long been known that the electrical resistance of alloys increases as the temperature is raised, but the want of a simple and accurate pyrometer has hitherto prevented experiments being carried far in this direction. Le Chatelier, however, has shown in a recent paper,† by the aid of his pyrometer, to be hereafter described, that in metals which do not undergo any molecular change before fusion, the increase of electrical resistance is proportional to the temperature. A great number of metals seem, like iron, to undergo sharply defined molecular changes at definite temperatures, and some alloys show progressive changes, all of which facts are clearly indicated by abrupt or gradual change in resistances.

The alloys as yet worked on are brass, German silver, and an

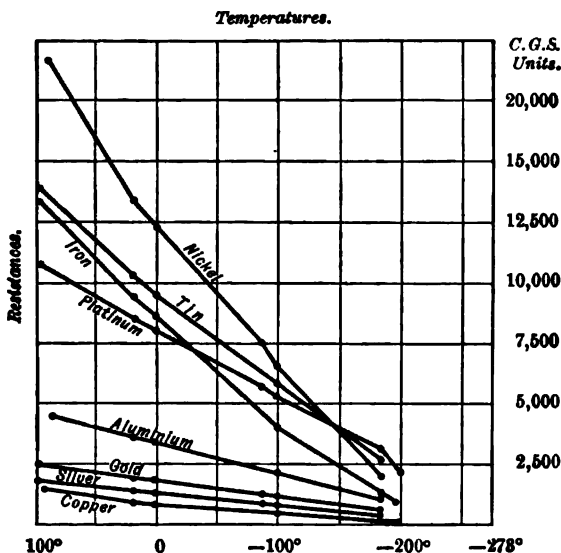
* *Report British Assoc.*, 1887, p. 341.

† *Comptes Rendus*, vol. cxi. (1890), p. 454.

alloy containing :—Copper, 70 per cent.; nickel, 18 per cent.; and iron, 11 per cent. These have been examined at temperatures between the ordinary temperature and their melting points.

Conduction of Electricity by Metals and Alloys at Low Temperatures

Professor Dewar has, as is well known, recently had at his command the means of producing intense cold, and by employing liquid oxygen has succeeded in working at so low a temperature as -200° C. He and Professor Fleming examined the electrical



resistances of metals and alloys at very low temperatures, and discovered the significant and important fact that the electrical resistances of *pure* metals decrease in such a manner as to suggest that if the absolute zero of temperature could be obtained the resistance would vanish.

It is remarkable that, as the experiments show, the electrical resistances of alloys do not diminish in the same manner, as will be seen by the accompanying diagrams. (Figs. 27a and 27b.)

* *Phil. Mag.*, vol. xxxiv. (1892), p. 326; vol. xxxvi. (1893), p. 271, in which some of the above results are slightly modified. See also *Engineer*, January 27, 1893.

Conduction of Electricity by Solid Alloys.—In the case of solid alloys—solidified solutions of metals, that is—the nature

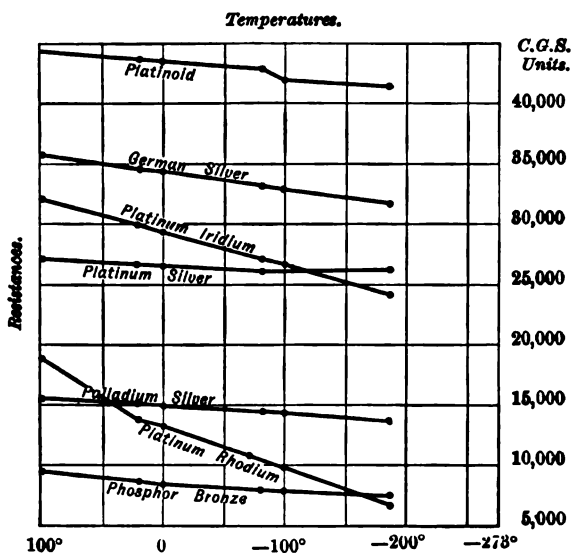
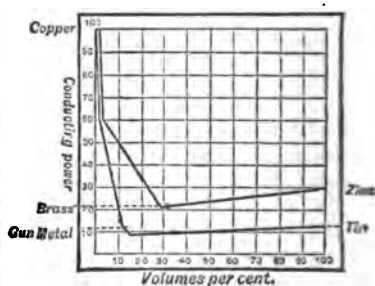
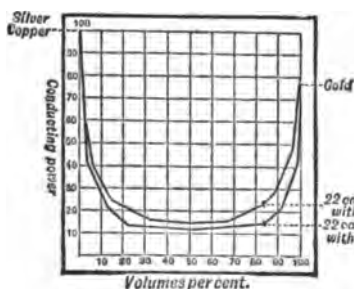


FIG. 27b.

of the evidence is very different, for the passage of the electric current through solid alloys reveals the existence 1st, of certain



well-defined compounds of the metals, and 2nd, renders it probable that in certain alloys the metals exist in allotropic states.

And here it is necessary to go back chronologically, and refer to the classical work of Matthiessen published in 1860.* He showed that the electrical conductivity of all alloys may be graphically represented by one or other of three typical curves,

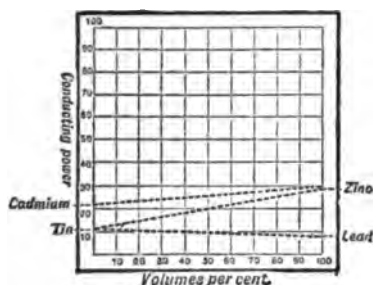


FIG. 30.

which, as the diagrams indicate, are respectively U-shaped (Fig. 28), L-shaped (Fig. 29), or straight lines (Fig. 30). On adding gold to silver, for instance, there is a rapid decrease of conductivity, silver being 100, and the curve gradually turns round and then rises without any break to the point representing the conductivity of gold.

In the case of the silver-copper series, silver being 100 and copper 96, there is a marked break in the U-shaped curve corresponding to the alloy, which contains 71.8 per cent. of silver, and this is probably a definite chemical alloy.

In the case of the L-shaped curve (Fig. 29), representing the conductivity of the copper alloys, SnCu_2 and SnCu_4 (which contain respectively 61.8 and 68.2 per cent. of copper) are probably definite compounds.† This view is confirmed by Laurie, who has shown quite recently by another‡ method—by determining the electromotive force of the copper series—that probably SnCu_2 is a chemically definite alloy.

The nature of the evidence is as follows :—

* *Phil. Trans. Roy. Soc.*, 1860, p. 161.

† See Roberts-Austen, *Phil. Mag.* [5], vol. viii. (1879), p. 551; and Lodge, *ibid.*, p. 554.

‡ *Journ. Chem. Soc.*, vol. liii., 1888, p. 104.

Laurie finds that if the zinc plate of a Daniell cell be replaced by a compound plate, formed by joining copper and zinc, the cell has the same electromotive force as one in which zinc alone is used. This is true even if the zinc surface be only $\frac{1}{1000}$ part of the copper surface. If the zinc plate be replaced by copper-zinc alloys, no deflection of the electrometer is observed as long as the alloy contains less than 67 per cent. of zinc. At this point however, a considerable deflection, practically equivalent to that given by zinc, is suddenly obtained. This result, in his opinion, may be taken as evidence of the existence of a compound of the two metals of the formula CuZn_2 . Alloys containing a greater proportion of zinc behave like zinc alone. Similarly, in the case of tin-copper alloys, a sudden rise of electromotive force is observed when the proportion of tin in the alloy exceeds that which would be contained in a compound of the formula SnCu_2 . This result is in harmony with the evidence already obtained by observations of the density and thermal and electrical conductivity of the copper-tin alloys. If an alloy containing a larger percentage of tin than SnCu_2 , in a state of fine division, be placed in a copper cup and used in place of the zinc in a cuprous chloride cell, the excess of tin is gradually eaten out, leaving approximately the alloy SnCu_2 . This alloy undergoes no change if the circuit be kept closed.

Fresh information has been gained as to the composition of these alloys by a series of cooling curves recently obtained in the author's laboratory (method described p. 151), which show their freezing points as affected by varying proportions of tin and copper. It was found that no alloy having as much as 4 per cent. of copper or 10 per cent. of tin had less than two distinct freezing points; and that some of these occurred at nearly the same temperature in different alloys; thus indicating the presence of fairly definite constituents, which, however, are not in general capable of existing by themselves, but only in the presence of an excess of one or the other of the metals.

Various investigators, including Wheatstone, Jules Regnault, Gauguain, Crova, Robb, Lindeck, and Hockin and Taylor, have examined the electromotive force of metallic amalgams in acid and saline liquids, and the latter investigators have shown that 1 part by weight of zinc in 23.6 million parts of mercury is electro-positive to pure mercury in a solution of zinc sulphate. Dr. G. Gore* employs two portions of very pure mercury as an electrolyte.

* *Chemical News*, vol. lxi. (1890), p. 40.

These are connected by insulated platinum wires with an ordinary astatic torsion galvanometer of 100 ohms resistance, and a sufficiently minute proportion of a very dilute amalgam, of known strength, of one of the particular metals with some of the same mercury is added to one of the portions of mercury, to cause the needles of the instrument to be just visibly deflected whilst being viewed with the aid of a magnifying glass. The following results were obtained:—

One Part of—	1.0 grain of HCl or H ₂ SO ₄ in 120 c.c. of Water—		20 grains of KCl in 120 c.c. of Water—	
	Parts of Mercury.		Parts of Mercury.	
Mg . . .	110,274,000,000	...	13,430,858,806	
Zn . . .	104,950,000,000	...	18,034,482,758	
Cd . . .	184,828,432	...	10,404,225	
Sn . . .	38,900,000	...	8,831,632	
Cu . . .	15,484,375	...	1,640,160	
Bi . . .	9,762,300	...	1,621,000	
Pb . . .	5,651,149	...	1,050,341	
Ag . . .	905	...	79	

The volume of water employed in each electrolyte was 120 c.c.

In the above table the order of voltaic energy of the metals is substantially the same as that of the metals alone and unamalgamated. With each amalgam the amount of energy gradually declined, but recovered on stirring the mixture; the decline was quickest with the most dilute ones.

Allotropic Modifications of Metals when Alloyed.—Of all the researches made by Matthiessen, some thirty years ago, none are of more interest at the present time than those which enabled him to obtain evidence as to the passage of metals from the normal state to an allotropic one, which sometimes attends their union with each other.

Turn, for instance, to the tin-copper curve; he points out that the decrement in the conductivity produced by the addition of a minute quantity of tin to copper is very rapid, and he urges that the amount of tin is far too small to permit the belief to be entertained that true chemical combinations had been formed, and by such reasoning he was led to his great generalisation, that metals may sustain change in their molecular condition by union with each other in a fused state. This is probably the most important generalisation which has hitherto been made in connection with the study of alloys. It may be well to begin the consideration of this question of the molecular change in metals, by a reference to some early views as to their constitution. Consider, therefore, a mass of antimony which is adorned with a

large crystalline star. An attempt to explain the origin of the star led Lemery to the conclusion "that the star doth proceed from the antimony itself; the purification of the metal does serve to lay open the crystals of antimony, and the iron (it contains) by its hardness does expatiate these crystals." This attempt to explain the development of a crystalline structure in a metal by the influence which the presence of a small quantity of a metallic impurity exerts, will serve as a fitting introduction to the class of facts now to be considered, the study of which has been much neglected, notwithstanding their importance in metallurgical industry. All that need be done is to adduce some evidence which may serve to throw light upon the question why a definite material actually employed in the manufacture of, say a bridge, or a weapon, can be depended on to perform the duty entrusted to it, and why a certain other material would be absolutely untrustworthy, although chemical analysis can barely show the difference between the two. It has long been known that the properties of a metal may be influenced by the presence of a minute quantity of another element, even though it is so small as to preclude the possibility of its action being due to the formation of an ordinary chemical compound to which any reasonable formula, based upon atomic proportions, could be assigned. It by no means follows, however, that the atom of the added element does not exert a direct influence, or that its action is not controlled by a well-known law, but it is clear that in the experiment about to be described, for instance, we are not dealing with the union of elements in atomic proportions. Take two ladles containing exceptionally pure bismuth, filled from the same crucible containing the molten metal, and into one ladle introduce a tiny fragment of tellurium. Pour the contents of both ladles into moulds, and when the metal is cold, fracture it. It will be seen that the bismuth to which the tellurium is added has become minutely crystalline, while that which remains pure has crystallised in broad mirror-like planes, and one reflects a ray of light like a mirror, while the other, which contains the tellurium scatters the light. If there were no other guide than that afforded by mere inspection, you would say that the two masses were totally distinct elementary substances, and yet the only difference is that one contains $\frac{1}{2000}$ part of tellurium, and the other does not.

There are many such facts to be met with in practical metallurgy, and the knowledge of them has been steadily accumulating for centuries, but it is only since the end of the last century that it can be said to have been built up on a scientific basis, for it

was not until 1781 that Bergman discovered the wonderful fact that the difference between wrought iron and steel depends upon the presence or absence of a small quantity of carbon. The smallness of the amount of carbon capable of producing such striking effects greatly astonished him, as well as the chemists who followed him, and repeated his experiments, but, strange as it may seem, the promulgation in 1803 of Dalton's atomic theory threw a flood of light upon chemical phenomena, but cast into shade such investigations as those of Bergman, which dealt with influences of traces upon masses, and the authority of Berthollet was not sufficient to save them from neglect. In this eventful year for science, 1803, the latter published his essay on chemical statics, in which he stated, as a fundamental proposition, that in comparing the action of bodies on each other, which depends "on their affinities and mutual proportions, the mass of each has to be considered."* His views were successfully contested by Proust, but, as Lothar Meyer says, the influence on chemistry of the rejection of Berthollet's views was remarkable. "All phenomena which could not be attributed to fixed atomic proportions were set aside as not truly chemical, and were neglected. The chemists forsook the bridge by which Berthollet had sought to unite the sister sciences, physics and chemistry." Fortunately, however, there was in this country one chemist who had followed up the line of work indicated by the early metallurgists, for in 1803, the same year as that in which Berthollet's essay was published, Charles Hatchett† communicated to the Royal Society the results of a research which he had conducted, with the assistance of Cavendish, in order to ascertain "the chemical effects produced on gold by different metallic substances when employed in certain" (often very small) "proportions as alloys."

The progress of research may show that it is possible, by a sufficiently high temperature, or by a suitable application of heat, to directly modify the chemist's atoms into which a molecule may be split up, and in this way to resolve one elemental substance into another; at present we only know with certainty that we can change the grouping of the atoms in a molecule, but cannot alter the atoms themselves. That such change in the grouping of atoms is possible has long been known.

It is now recognised that, except in the case of unstable forms of elements, the occurrence of elements in different allotropic states means that, in the respective cases, the atoms are differently arranged in the molecules of which the body is composed.

* English edition, by M. Farrell, M.D., 1804, p. 5.

† *Phil. Trans.*, vol. xciii. (1803), p. 43.

These definitions need not be dwelt upon here; it is only necessary to point out the great industrial importance of the change in the molecular conditions of metals and alloys, produced, as these changes are, by comparatively slight influences.

Chemists have, even to the present day, been very slow to examine the conditions under which a metal, when pure, can exhibit widely different properties, can pass from one allotropic state, as it is termed, to another. Berzelius claimed that the metals osmium and iridium could exist in different allotropic states; and in 1846, Joule and Lyon Playfair,* showed that certain metals in different allotropic states possessed different volumes; and although chemical analysis could detect no change in the composition of a particular metal in either of its different states, its properties were widely different. There are several instances of this. In 1849 Bolley prepared lead by electrolysis. It is similar in composition to sheet lead; but Bolley's lead oxidises rapidly in air, and becomes converted into a yellow powder, and sheet lead does not. There is a form of copper which was first prepared in 1878 by Schützenberger, its specific gravity is less than that of ordinary copper, it oxidises rapidly in air, its behaviour in relation to nitric acid is different from that of ordinary copper, and last, it may be converted into ordinary copper by prolonged contact with dilute sulphuric acid. Similar cases of allotropy are claimed by Fritsche for tin, and by Schützenberger,† for silver. It is not necessary to allude specially to Gore's antimony, or to modifications of nickel and palladium, because in their cases the passage from one state to another is determined by the presence or absence of occluded gas, and therefore the phenomenon becomes more complicated than when the composition of the metal is unchanged. It is quite true that in the cases referred to the variations in properties—the allotropy of the same element—are far less marked than the variations which characterise isomerism of organic compounds, but they are nevertheless very real and important, and if we knew the metals mentioned only in their unstable conditions, they would be unfit for industrial use.

Fritsche found that certain ingots of tin, when exposed to the rigour of a Russian winter, fell into powder. This powder was certainly an allotropic form of tin; it was grey and needle-like, but by heating to a point far below its melting point, it became changed into ordinary tin; and Fritsche points out that this property which tin possesses of passing into an unusual condition

* *Memoirs of the Chem. Soc.*, vol. iii. p. 57.

† *Bull. Soc. Chim.*, vol. xxx. (1878), p. 3.

led on one occasion to some difficulty. A quantity of buttons, consisting mainly of tin, and intended for the adornment of military uniforms, were safely delivered by the manufacturer and placed in store. On inspection, however, the military authorities, found nothing but a shapeless mass of grey powder, for the tin had assumed its allotropic form, and the buttons had disappeared.

We may now consider the question—Do metals, when they enter into union with each other, preserve their normal conditions, or do they ever assume allotropic states? The experimental evidence that they do assume such states is difficult to obtain, but some facts relating to this subject may be stated.

Evidence is not wanting of allotropy in metals released from solid alloys. Certain alloys may be viewed as solidified solutions, and when such bodies are treated with a suitable solvent, usually an acid, it often happens that one constituent metal is dissolved, and the other released in an insoluble form. For example, if a fragment of an alloy of potassium and gold containing about 10 per cent. of the precious metal, be thrown upon water, the potassium takes fire, decomposes the water, and the gold is released as a black powder; this black or dark-brown gold is an allotropic modification of gold, as there is evidence that it combines with water to form auric hydride. By heating this dark gold to dull redness, it at once assumes the ordinary golden colour. The Japanese use this gold, released from gold-copper alloys, in a remarkable way, for they produce by the aid of certain pickling solutions, a beautiful purple patina on copper, which contains only 2 per cent. of gold, while even a trace of the latter metal is sufficient to alter the tint of the patina.

Joule proved that when iron is released from its amalgam by distilling away the mercury, the metallic iron takes fire on exposure to air, and is therefore clearly different from ordinary iron and is, in fact, an allotropic form of iron. Moissan* has shown that similar effects are produced in the case of chromium manganese, cobalt and nickel, when released from the amalgams with mercury.

The best illustration of the change produced in a metal by the action of mercury is afforded by the following experiment. A plate of metallic aluminium would long remain exposed to air without sensible oxidation. Mercury also does not oxidise at the ordinary temperature, when exposed to air, but if the surface of the plate of aluminium be covered with a layer of mercury, then oxidation rapidly ensues, and the plate will soon become covered

* *Comptes Rendus*, vol. lxxxviii. (1879), p. 180.

with a white film of alumina, which may be detached in flakes. Clearly the condition of the aluminium has been modified by its association with the mercury.

It has already been stated that water can be frozen by cold produced by the solution of finely divided fusible-metal in mercury. It is not a matter of indifference whether the powders of the mixed constituents of the alloy are employed, or whether the alloy is previously prepared by fusion, and then powdered, which shows that the act of fusion has effected some change in the molecular arrangement of the metals. The explanation of the depolymerisation of the metals when they are united with each other is somewhat complicated. First, Mazetto* has shown that there is a similar lowering of temperature, though to a far less extent, when molten tin is mixed with molten lead, so that the lowering of the temperature is by no means confined to the solution of metals in mercury. The next step we owe to Professor W. Spring, of Liège, whose results in building up alloys by compressing the powders of their constituent metals have already been referred to. Spring finds that by determining the amount of heat given out by alloys of lead and tin on cooling from a molten state, that more heat is actually given out than might be expected from the results of calculation;† the difference is so great that it could not be due to errors of observation, for in actual numbers it amounts to many hundreds of calories for a weight of 100 grammes. He concludes that when molten tin is added to molten lead, the atomic constitution of the molecules is simplified—that is, depolymerisation takes place. Let it be assumed that each molecule of molten lead contains an arbitrary number of atoms, say five, and that the molecule of molten tin also contains five atoms. Then, if one molecule of lead be added to three molecules of tin, so as to form the alloy $PbSn_3$, five groups of $PbSn$, will be the result, but each molecule of the alloy will contain four atoms instead of five. This molecular change requires heat to effect the re-arrangement in the molten admixture of metals, and as this heat is absorbed cold is produced, and it will therefore be evident that both theory and experiment tend to the view that molecular change may be produced by alloying metals.

Debray‡ has given a case of an alloy in which a simple elevation of temperature induces allotropic change in the constituent metals. It is prepared as follows:—95 parts of zinc are alloyed by fusion with 5 parts of rhodium, and the alloy is treated with hydrochloric

* *Rendiconti del R. Istituto Lombardo* [2], vol. xviii., No. 3.

† *Bull. de l'Acad. Roy. de Belgique* [3], vol. xi., No. 5, 1886.

‡ *Comptes Rendus*, vol. xc. (1880), 1195.

acid, which dissolves away the bulk of the zinc, leaving a rich rhodium-zinc alloy, containing about 80 per cent. of rhodium. When this alloy is heated *in vacuo* to a temperature of 400° C., a slight explosion takes place, but no gas is evolved, and the alloy is then insoluble in *aqua regia*, which dissolved it readily before the elevation of temperature caused it to change its state. We are thus presented with another undoubted case of isomerism in alloys, the unstable, soluble modification of the alloy being capable of passing into the insoluble form by a comparatively slight elevation of temperature.

Influence of Varying Quantities of Metals on Each Other.—There is, undoubtedly, a firm experimental basis for the view to which Matthiessen was guided, nearly thirty years ago, by a study of the electrical resistance of solid alloys, that when metals are united to form alloys, in many cases one metal, and sometimes both metals, assume the allotropic state. He showed, for instance, that silver has a conductivity represented by 100, and that the addition of a small quantity of gold to the silver is attended with a rapid fall in the conducting power. The conductivity of pure copper may be represented by the number 98, the addition of a small portion of tin greatly diminishes the conductivity, as is proved by the curves given on p. 68. He pointed out that the amount of tin is too small to admit of the possibility of a chemical compound being formed, and from this fact and other evidence he concludes that the passage to an allotropic state can alone explain the result. In this connection the influence of small quantities of one element on large masses of another may be referred to. Submarine telegraphy will present us with the first case. The commercial success of a submarine cable is measured by the speed with which messages can be sent through it, and upon this point we have the testimony of Preece, who tells us that a cable made with the copper of to-day, when the necessity for using pure copper is recognised, will carry twice the number of messages that a similar cable of less pure copper would in 1858, when the influence of impurities in increasing the electrical resistance of copper was not understood. A paper by Lord Kelvin * shows how very important the purity of copper is, and how remarkable is the action of the impurity. It is safe to say that the presence of 0.1 per cent. of bismuth in the copper would, by reducing its conductivity, be fatal to the commercial success of the cable.

The influence of small quantities of foreign matter is more marked in the case of iron, but this question may be more conveniently studied in the following chapter.

* *Proc. Roy. Soc.*, vol. x. (1860), p. 301.

With regard to gold, the addition of 0.2 per cent. by weight of bismuth would, from the point of view of coinage, convert the gold into a useless material, which would crumble under the pressure exerted through the die. Instances of a similar nature might be multiplied indefinitely; it will, however, be sufficient to quote a statement of Sir Hussey Vivian, who says that $\frac{1}{1000}$ part of antimony will convert the best selected copper into the worst conceivable.

In order to explain facts such as these, it is necessary to ascertain what relations may subsist between the atoms of a mass of metal and the atoms of the added impurity. First, as regards the cohesion of a metal, this property may be investigated by the aid of heat, or by submitting the metal to mechanical stress; and, in a research to which the author* devoted much time, tenacity was selected as the property to be tested, with a view to ascertain the effect of the added matter upon a metal or alloy. Gold was chosen as the subject of the experiment for the following reasons:—First, it is a metal which it is possible to purify in a very high degree, it is not liable to oxidation, and the accuracy of the results is not affected by the presence of occluded gases. The purest gold has a tenacity of 7 tons to the square inch, and it elongates about 30 per cent. before breaking. Standard gold, which contains over 91 per cent. of gold, the alloying metal being copper, has a tensile strength of 18 tons to the square inch, and it stretches 34 per cent. before breaking; in fact, when an eminent engineer saw the results of these tests, he expressed an opinion as to the possibility of making a very good gun of standard gold, if the cost of the material were no object. When, however, a small quantity of certain metals, 0.01, 0.1, or 0.2 per cent. is added to the gold, the cohesion of the metal is reduced in a very remarkable way, as Hatchett showed to be the case in 1803. The author has tried the effect of adding to pure gold various metals and metalloids, introducing in each case 0.2 per cent. Some of these elements reduced the tenacity and extensibility of gold to a very low point, while others increased one or both of these properties. Since 1826, when Gmelin called attention to the relations between the atomic weights of elements which have similar properties, chemists have been actively engaged in establishing analogies between the properties of the elements and in arranging them systematically, and the result has been (mainly through the labours of Newlands, Mendeléeff, and Lothar Meyer) the promulgation of the Periodic law. This law states that the properties of

* *Proc. Roy. Soc.*, vol. xliii. (1888), p. 425; and *Phil. Trans.*, vol. clxxix. (1888), A., p. 339.

the elements are a periodic function of their atomic weights. Lothar Meyer has gone further, and has shown that a remarkable relation exists between the atomic volumes of the elements. Now, however tiny the atoms may be, they must possess volume, and the volume of each element will be peculiar to itself. The space occupied by one atom cannot yet be measured absolutely, but relative measurements may be obtained "by taking such quantities of the elements as are proportional to their atomic weights, and comparing the space occupied by these quantities." The relative atomic volumes of the elements are found by dividing the atomic weights of the elements by their specific gravities. The atomic weight of gold is 196.2; $\frac{196.2}{19.3} = 10.2$ the atomic volume,

or, expressed in the metric system, 196.2 grammes of gold would occupy a space of 10.2 cubic centimetres. Lead, on the other hand, would have the large atomic volume of 18.1 and potassium that of 45.1. The question now arises—Does the power to produce fragility, which we have seen certain elements to possess, correspond to any other of their properties by which they may be classified? The facts represented in the Periodic law were, in 1869, graphically represented by Lothar Meyer in his well-known curve of the elements. By adopting atomic weights and atomic volumes as co-ordinates he showed that the elements can be arranged in a curve representing a series of loops, the highest points of which are occupied by caesium, rubidium, potassium, sodium, and lithium, whilst the metals which are most useful for industrial purposes occupy the lower portions of the several loops.

An examination of the results the author has obtained shows that not a single metal or metalloid which occupies a position at the base of either of the loops of Lothar Meyer's curve diminishes the tenacity of gold. On the other hand, the fact is clearly brought out that metals which render gold fragile all occupy high positions on the curve. This would appear to show that there is some relation between the influence exerted by the metallic and other impurities and either their atomic weights or their atomic volumes. It seems hardly probable that it is due to atomic weight, because copper, with an atomic weight of 63.2, has nearly the same influence on the tenacity of pure gold as rhodium, with an atomic weight of 104, or as aluminium, the atomic weight of which is 27.0. It will be evident from the following table, which embodies the results of the author's experiments, that metals which diminish the tenacity and extensibility of gold have high atomic volumes, while those which increase these properties have either the same atomic volume as gold, or a

lower one. Further, silver has the same atomic volume as gold, 10.2, and its presence in small quantities has very little influence, one way or the other, on the tenacity or extensibility of gold.

Name of added Element.	Tensile Strength. Tons Per Sq. In.	Elongation, Per Cent. (on 3 inches).	Impurity Per Cent.	Atomic Volume of Impurity.
Potassium .	Less than 0.5	Not perceptible	Less than 0.2	45.1
Bismuth .	0.5 (about)	"	0.210	20.9
Tellurium .	3.88	"	0.186	20.5
Lead .	4.17	4.9	0.240	18.0
Thallium .	6.21	8.6	0.193	17.2
Tin .	6.21	12.3	0.196	16.2
Antimony .	6.0 (about)	97.	0.203	17.9
Cadmium .	6.88	44.0	0.202	12.9
Silver .	7.10	33.3	0.200	10.1
Palladium .	7.10	32.6	0.205	9.4
Zinc .	7.54	28.4	0.205	9.1
Rhodium .	7.76	25.0	0.21 (about)	8.4
Manganese .	7.99	29.7	0.207	6.8
Indium .	7.99	26.5	0.290	15.3
Copper .	8.22	43.5	0.193	7.0
Lithium .	8.87	21.0	0.201	11.8
Aluminium .	8.87	25.5	0.186	10.6

These results are shown graphically in the diagram (Fig 31). The tenacity of pure gold is 7 tons per square inch.

INFLUENCE OF IMPURITIES ON GOLD.

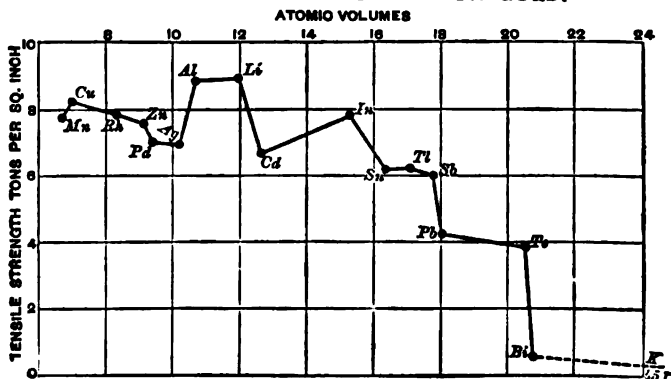


FIG. 31.

Several of the elements, the action of which has been examined, occupy abnormal positions, and any reason for this, except allotropy, remains to be explained. It is difficult to offer any mechanical theory to account for the action of the elements, but it may perhaps be well to give a rough indication of what may take place. If five spheres, representing atoms of a certain volume, are arranged in one plane so as to touch each other, then the addition of an element with a small atomic volume may improve the tenacity by filling up the central space which would otherwise remain void; with such an arrangement of five atoms the addition of an element with the same atomic volume as themselves will tend to drive them slightly further asunder, and should, therefore, act prejudicially in a five-atom group, although it would exactly fill the space between a six-atom group, but in either case the insertion of a larger atomic volume than that of each member of the group, must tend to drive the members of either the five or six-atom group further asunder, and by so doing would diminish the cohesion of the mass. No doubt, in some cases, condensation takes place, and this may explain some of the abnormal results.

The curve representing the extensibility of the gold to which impurities have been added resembles that shown in Fig. 31. Cadmium exhibits marked irregularity in both curves; but the only striking difference between the two curves is caused by tellurium and bismuth, the former of which seems to be more prejudicial to the elongation of gold than to its tenacity. The influence of cadmium in increasing the extensibility is very remarkable. Aluminium, indium, and lithium occupy somewhat abnormal positions on the curve of tenacity, for they possess high atomic volumes, and yet they appear to increase the tenacity of gold, although they reduce its capability of being elongated. The author has some researches in progress, the results of which appear to enable this abnormal behaviour to be explained (see pp. 169, 177.)

With regard to the applicability of these generalisations to other metals, it may be observed that recent investigations of Hadfield as to the physical properties of aluminium-steel, show that the part played by aluminium is almost identical with that of silicon, and this fact strongly supports the view above stated, for it is remarkable that the two bodies, aluminium and silicon, of which, when in a free state, the physical and mechanical properties are totally different, should nevertheless when they are alloyed with iron affect it in precisely the same way. Silicon and aluminium have almost the same atomic volume.

Questions of great industrial interest present themselves, espe-

cially in connection with iron. With regard to this metal, the evidence as to the action of other elements upon it tends in the same direction as in the case of gold, although the question is greatly complicated by the relations of iron to oxygen, and by the presence of occluded gases.

In the case of iron, it is difficult to say what property of the metal would be most affected by the added matter; but the author pointed out, in a lecture delivered at Newcastle in 1889, that the direct connection with the Periodic law will probably be traced by the effect of a given element in retarding or promoting the passage of ordinary iron to the allotropic state, a point of much importance, as the mechanical properties of the metal must depend on the atomic arrangement in the molecules. Osmond* has since satisfied himself of the accuracy of this view. He considers, as will be shown in the following chapter, that there are two modifications of iron; the α , or soft variety, which exists in pure iron at temperatures below 855°C ., and in iron containing certain other elements, if it has been cooled slowly. There is also the β , or hard modification, which exists at high temperatures or if certain elements be present, in iron which has been rapidly cooled from temperatures above 855°C ., or if the iron has been obtained by electrolysis.

The foreign elements, whose action on the critical points of iron has been studied by Osmond experimentally, are ranged as follows in two columns in the order of their atomic volumes:—

I.				II.			
Carbon .	.	.	3.6	Chromium .	.	.	7.7
Boron .	.	.	4.1	Tungsten .	.	.	9.6
Nickel .	.	.	6.7	Silicon .	.	.	11.2
Manganese .	.	.	6.9	Arsenic .	.	.	13.2
Copper .	.	.	7.1	Phosphorus .	.	.	13.5
				Sulphur .	.	.	15.7

The elements in column I., whose atomic volumes are smaller than that of iron (7.2), delay during cooling the change of the β , or hard allotropic variety of iron, into the α , or soft variety, as well as that of hardening carbon into carbide carbon. For these two reasons they tend to increase, with equal rates of cooling, the proportion of β iron that is present in the cooled iron or steel, and consequently the hardness of the metal. Indeed, their presence is equivalent to a more or less energetic hardening. To these elements hydrogen may be added. As is well known, this element renders electro-deposited iron hard and brittle; perhaps.

* *Comptes Rendus*, vol. cx. (1890), p. 346.

it contains the metal, Graham's *hydrogenium*, for hydrogen gas does not appear to have a marked influence on the critical temperature.

The elements in column II., whose atomic volumes are greater than that of iron, tend to raise or at least maintain near its normal position, during cooling, the temperature at which the change of β to α iron takes place. Further, they render the inverse change during heating more or less incomplete, and usually hasten the change of "hardening carbon" to "carbide carbon." Thus, they maintain the iron in the α state at high temperatures, and must therefore have the same effect in the cooled metal. In this way, they would act on iron as annealing does, rendering it soft and malleable, did not their individual properties, or those of their compounds, often intervene and partially mask this natural consequence of their presence.

Thus, foreign elements alloyed with iron either hasten or delay the passage of the iron, during cooling, to an allotropic state, and render the change more or less incomplete, according to whether the atomic volume of the added impurity is less or greater than that of iron. In other words, foreign elements of low atomic volume tend to make iron itself assume or retain the particular molecular form that possesses the lowest atomic volume, whilst elements with large atomic volume produce the inverse effect.

While obeying the general law, carbon possesses on its own account the property of undergoing, at a certain critical temperature, a change, the nature of which is still disputable, although its existence is acknowledged. This property gives carbon a place by itself in the metallurgy of iron.

Whatever may ultimately prove to be the true nature of the molecular change which accompanies the thermal treatment of iron and determines its mechanical properties, there is little doubt but that there is a close relation between the action of foreign elements and their atomic volume. Few metallurgical questions are of greater interest at the present time than those which relate to the molecular structure of metals, and Osmond has shown it to be very probable that the presence of a small quantity of a foreign metal may cause a mass of another metal to pass into an allotropic state. In relation to iron and steel the problems are of great industrial importance, and it is fortunate that we appear to be nearing the discovery of a law in accordance with which *all* metallic masses are influenced by "traces."

The effect of comparatively large quantities of certain elements on the mechanical properties of iron has already been stated in Chapter II., and will be again referred to in Chapter IV.

Colour of Alloys.—It will now be well to examine some effects of uniting metals by fusing them together, and also to consider the direct influence of a minute quantity of one metal in changing the mass of another in which it is hidden, causing it to behave in a different way in relation to light, and consequently to possess a colour different from that which is natural to it. The added metal may so change the chemical nature of the metallic mass that varied effects of colour may be produced by the action of certain "pickling" solutions. This portion of the subject is so large that reference can only be made to certain prominent facts.*

First, with reference to the colour produced by the union of metals. Take, for example, a mass of red copper, and one of grey antimony; the union of the two by fusion produces a beautiful violet alloy when the proportions are so arranged that there is 51 per cent. of copper, and 49 per cent. of antimony in the mixture. This alloy was well-known to the early chemists, but, unfortunately, it is brittle and difficult to work, so that its beautiful colour can hardly be utilised in art. The addition of a small quantity of tin to copper hardens it, and converts it, from a physical and mechanical point of view, into a different metal. The addition of zinc and a certain amount of lead to tin and copper, confers upon the metal copper the property of receiving, when exposed to the atmosphere, varying shades of deep velvety brown, characteristic of the bronze which has from remote antiquity been used for artistic purposes. But by far the most interesting copper-alloys, from the point of view of colour, are those produced by its union with zinc, namely brass. Their preparation demands much care in the selection of the materials.

The most remarkable case known of a coloured alloy, is that recently published by the author† who found that gold alloyed with 10 per cent of aluminium is brilliantly white, but from this point as aluminium is added the tint deepens until flecks of pink appear, and when 78 parts of gold are added to 22 parts of aluminium, an intensely ruby-coloured alloy, AuAl_2 , is obtained.

The colouring power of metals in alloys is very variable. Ledebur ‡ arranges the principal metals in the following order:—Tin, nickel, aluminium, manganese, iron, copper, zinc, lead, platinum, silver, gold.

Each metal in this series has a greater decolorising action than the metal following it. Thus, the colours of the last members are

* A list of books and papers dealing with the colours of metals and alloys, and with the production of coloured patina, is given by Professor Ledebur in his work *Die Metallverarbeitung*, 1882, p. 285.

† *Proc. Roy. Soc.*, vol. xlix., 1891, p. 347.

‡ *Loc. cit.*, p. 51.

concealed by comparatively small amounts of the first members. A good example is afforded by the alloy used for the continental nickel coinage. This consists of three parts of red copper with only one part of white nickel. The comparatively small quantity of nickel is, however, sufficient to completely hide the red colour of the copper.

Of the very varied series of alloys the Japanese employ for art metal-work, the following may be considered the most important and typical. The first is called *shaku-do*, it contains, as will be seen from Analyses Nos. I. and II.,* in addition to about 95 per cent. of copper, as much as 4 per cent. of gold. The quantity

	I.	II.
Copper	94.50 ...	95.77
Silver	1.55 ...	0.08
Gold	3.73 ...	4.16
Lead	0.11 ...	—
Iron and Arsenic	traces ...	—
Totals	99.89 ...	100.01

of gold is, however, very variable, some specimens which have been analysed containing only 1.5 per cent. of the precious metal.

Another important alloy is called *shibu-ichi*. Analyses of this alloy gave:—

	III.	IV.
Copper	67.31 ...	51.10
Silver	32.07 ...	48.93
Gold	traces ...	0.12
Iron	0.52 ...	—
	99.90	100.15

There are numerous varieties of it, but in both these alloys, *shaku-do* and *shibu-ichi*, the point of interest is that the precious metals are, as it were, sacrificed in order to produce definite results, gold and silver, when used pure, being employed very sparingly to heighten the general effect. In the case of the *shaku-do*, we shall see presently that the gold appears to enable the metal to receive a beautiful, rich purple coat or patina, as it is called, when treated with certain pickling solutions; while *shibu-ichi* possesses a peculiar silver-grey tint of its own, which, under ordinary atmospheric influences, becomes very beautiful, and to which the Japanese artists are very partial. These are the principal alloys, but there are several varieties of them, as well as combinations of *shaku-do* and *shibu-ichi* in various proportions, as, for instance, in the case

* Analyses Nos. I. and III. are by Mr. Gowland, of the Imperial Japanese Mint at Osaka; Nos. II. and IV., by Prof. Kalischer, *Dingl. Polyt. Journ.*, vol. ccxv. p. 93.

of *kiu-shibu-ichi*, the composition of which would correspond to one part of *shaku-do*, rich in gold, and two parts of *shibu-ichi*, rich in silver.

Now, as to the action of pickling solutions.

The Japanese art metal-workers are far ahead of their European brothers in the use of such solutions.

The South Kensington Museum contains a very valuable series of fifty-seven oblong plates, some plain and others richly ornamented, which were specially prepared as samples of the various metals and alloys used by the Japanese. The Geological Museum in Jermyn Street has a smaller, but more instructive, series of twenty-four plates, presented by an eminent metallurgist, the late Mr. Hochstätter-Godfrey. From descriptions accompanying the latter, and from information gathered from certain Japanese artificers, it would appear that there are three solutions generally in use. They are made up respectively in the following proportions, and are used boiling :—

	I.	II.	III.
Verdigris . . .	438 grains	87 grains	220 grains
Sulphate of copper . .	292 "	437 "	540 "
Nitre . . .	—	87 "	—
Common salt . . .	—	146 "	—
Sulphur . . .	—	233 "	—
Water . . .	1 gallon	—	1 gallon
Vinegar . . .	—	1 gallon	5 fluid drachms

The most widely employed is No. I. When boiled in No. III. solution pure copper will turn a brownish-red, and *shaku-do*, which contains a little gold, becomes purple. Thus, it is possible to appreciate the effect of small quantities of metallic impurity as affecting the colour resulting from the action of the pickle. Copper containing a small quantity of antimony gives a shade very different from that resulting from the pickling of pure copper. But the copper produced in Japan is often the result of smelting complex ores, and the methods of purification are not so perfectly understood as in the West. The result is that the so-called "antimony" of the Japanese art metal-workers, which is present in the variety of copper called *kuromi*, is really a complex mixture containing tin, cobalt, and many other metals, so that a metal-worker has an infinite series of materials at command with which to secure any particular shade; and these are used with much judgment, although the scientific reasons for the adoption of any particular sample may be hidden from him. It is strictly accurate to say that each particular shade of colour is the result of minute quantities of metallic impurity.

There is one other material to the production of which art-

workmen in this country will, it is to be hoped, soon direct their attention, as the possibilities of its applications are endless. It is called in Japanese *mokumé*, which signifies "wood grain." It is now very rare, even in Japan, but formerly the best specimens appear to have been made in Nagoya by retainers of the Daimio of Owari.

This diagram (Fig. 32) shows the method of manufacture.

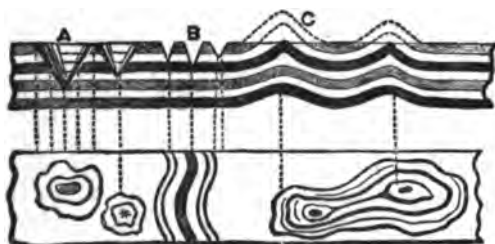


FIG. 32.

Take thin sheets of gold, silver, *shibu-ichi*, *shaku-do*, and *kuromi*, and solder* them together, layer upon layer, care being taken that the metals which will present diversity of colour come together. Then drill conical holes of varying depth (A) in the mass, or devices in trench-like cuts of V section (B), and then hammer the mass until the holes disappear; the holes will thus be replaced by banded circles and the trenches by banded lines. Similar effects may be produced by taking the soldered layers of the alloy, and, by the aid of blunted tools, making depressions on the back of the mass, so as to produce prominences on the front (C). These prominences are filed down until the sheet is again flat; the banded alloys will then appear on the surface in complicated sections, and a very remarkable effect is produced, especially when the colours of the alloys are developed by suitable "pickles." In this way any device may be produced. In principle the method is the same as that which produces the damascening of a sword-blade or gun-barrel, and depends on the fact that, under certain conditions, metals behave like viscous solids, and as truly "flow" as pitch or honey does. In the case of *mokumé* the art-workman has a wide range of tinted metals at command.

The Oriental art metal-workers often blend metals and alloys of different colours by pouring them together at a temperature near the solidifying point of the more infusible of the metals and

* The following solder was found to answer well :—Silver, 55.5; zinc, 26.0; copper, 18.5.

alloys to be associated. In this way, by pouring the comparatively fusible grey silver-copper alloy on to fused copper which is just at the point of "setting," the metals unite, but do not thoroughly mix, and a mottled alloy is produced. The Japanese use such alloys in almost every good piece of metal-work.

Alloys of Industrial Importance.—The following tables indicate the composition of some of the more important alloys, which have been selected in order to give the student an idea of the way in which for industrial use metals are associated. The list is, however, necessarily a limited one, and as the properties of an alloy may be greatly modified by a slight variation in its composition, reference should be made for fuller information to the standard treatises, of which a list is appended:—R. H. Thurston, Report on a Preliminary Investigation of the Properties of the Copper-Tin Alloys, Washington, 1879; A. Guettier, *Guide Pratique des Alliages Métalliques*, Paris, 1865; Roberts-Austen, The Alloys used for Coinage (Cantor Lectures, Society of Arts), 1884; A. Ledebur, *Metallverarbeitung*, Brunswick, 1882; Brannt, Krupp, and Wildberger, "The Metallic Alloys," Philadelphia, 1880. *Proc. Inst. Mech. Engineers*, 1891, 1893.

Of recent years, bronzes have come largely into use, in which a minute quantity of a foreign element has been added. The oldest of these bronzes, phosphor bronze, invented by Dr. Kuntzel, is now in general use for the manufacture of machine parts. The presence of phosphorus usually renders bronze brittle, but when added only in sufficient quantity to reduce the oxide contained in the metal, it imparts hardness to the alloy without brittleness. The phosphorus varies up to 2 to 4 per cent., and it has been asserted that the presence of phosphorus is useful in enabling bronzes to be made richer in tin than would otherwise be the case. Manganese bronze has a tensile strength of 29 tons per square inch (annealed rolled rods) to 39 tons (cold rolled). Owing to its non-liability to corrosion it is well adapted for the manufacture of propellers. Silicon bronze is well adapted for telegraphic purposes. The first sample, of which an analysis is given, (telegraph wire) had a tensile strength of $28\frac{1}{2}$ tons per square inch, and a conductivity of 98; the second (telephone wire) a tensile strength of $52\frac{3}{4}$ tons per square inch and a conductivity of 43; the tensile strength of copper being 17 tons per square inch, and its conductivity 100. Delta metal, is a yellow alloy, with a specific gravity of 8.4, and a melting point of 1800° F. Cast in sand it has a tensile strength of 2 tons per square inch, and when hammered or rolled cold it has a tensile strength of 40 tons per square inch.

—		Copper	Zinc	Tin	Other Constituents	Uses and Remarks.
Brass	. . .	63 to 72	27 to 34	—	Pb 0.28 . . .	Typical brass.
"	. . .	70.29	29.26	0.17		Wire. Always brittle if Pb reaches 2 per cent. Tin may vary from 0.1 to 0.5.
Muntz's metal	. . .	60 to 62	38 to 40	—	Fe 4.66 . . .	Ships' sheathing.
Sterro metal	. . .	55.33	41.80	—	Fe 1.5 . . .	Austrian, for ordnance.
Aich's metal	. . .	60.00	38.12	—		English. Sterro and Aich's metals are remarkable for their great strength, 85,080 lbs. per sq. in.
Mosaic gold	. . .	65.00	35.00	9.00		For ordnance.
Pinchbeck	. . .	83.33	16.76	23.50		"Big Ben," Westminster.
Mannheim gold	. . .	80 to 88	20 to 12	25.2	Fe, Ni, traces . . .	Telescope mirror, Birr Castle, Ireland.
Gun metal	. . .	91.00	—	29.11		
Bell metal	. . .	76.50	—			
"	. . .	75.8	trace			
Speculum metal	. . .	70.24				
"	. . .	66.6	—	33.4		
"	. . .	68.1	—	31.9		
Bronze	. . .	95.0	1.0	4.0		Ross. Atomic proportion.
"	. . .	82.7	1.8	4.7		British bronze coinage.
"	. . .	71.4	6.0	5.9	Pb 9.9 . . .	Japanese art bronze.
"	. . .	74.0	10.0	1.0	Pb 16.3 . . .	"
"	. . .	83.5	—	5.15	Pb 15.0 . . .	Chinese art bronze.
"	. . .	94.0	—	5.90	Pb 8.3; Fe 3 . . .	Prehistoric sword (Ireland).
"	. . .	88.46	—	10.04	Fe 0.1 . . .	Egyptian chisel.
"	. . .	80 to 90	7.0	18 to 12	Pb 1.5 . . .	Attic coin.
Aluminium bronze	. . .	90.00	—	—	Al 10.0 . . .	Bearings for heavy axles.
Phosphor bronze	. . .	82.20	—	12.95	Pb 4.28; P 0.52	Tensile strength, 96,434 lbs. per sq. in.
Manganese bronze	. . .	83.45	—	—	Mn 13.48; Fe 1.24; Co 0.11	Yellowish grey.
"	. . .	81.03	—	—	Mn 16.86; Fe 1.67; Co 0.06	Yellowish white.
Silicon bronze	. . .	99.94	—	0.03	Fe, Si trace . . .	Telegraph wire.
"	. . .	97.12	1.12	1.14	Fe trace . . .	Telephone "
Delta metal	. . .	55.10	43.47	—	Fe 1.08; Pb 0.37; P 0.10	

COPPER NICKEL ALLOYS.

—	Cu.	Ni.	Zn.	Other Constituents.	Remarks.
Nickel coins .	75.0	25.0			
Packfong . .	43.8	15.6	40.6	—	Chinese alloy.
English "German silver" .	61.3	19.1	19.1		
Berlin argentan	52.0	26.0	22.0		
Sheffield German silver .	57.0	24.0	19.0		
Platinoid . .	—	—	—	A German silver, with 1 to 2 per cent. of tungsten.	High electrical resistance, not changing with temperature.
Ancient coin .	77.58	20.0	—	Fe 1.04; Co 0.54; Sn 0.03.	Second century, B.C.

TIN ALLOYS.

—	Sn.	Sb.	Cu.	Other Constituents.	Remarks.
Britannia metal	90.62	7.81	1.46		
White metal .	82.00	12.00	6.00		Birmingham sheet. For bearings. The composition of white metal is very variable.
" .	53.00	10.60	2.40	Pb 33.0; Zn 1.0.	
Ashberry metal	77.8	19.4	—	Zn 2.8.	
Pewter . . .	80.0	—	—	Pb 20.0.	
Solder, fine . .	66.6	—	—	Pb 33.3	The melting point increases with the proportion of lead.
" tin . .	50.0	—	—	Pb 50.0.	
" plumbers'	33.3	—	—	Pb 66.6	Authorized by the Plumbers' Company.

LEAD ALLOYS.

—	Pb.	Sb.	Sn.	Other Constituents.	Remarks.
Type metal . .	70.0	18.0	10.0	Cu 2.0.	For stereotyping. For slowly revolving axles.
" . .	82.0	14.8	3.2	—	
Bearing metal .	84.0	16.0	—	—	
Shot metal . .	60.0	20.0	20.0	As 0.2 to 0.35	
	99.6	—	—		

ZINC ALLOYS.

—	Zn.	Sn.	Cu.	Other Constituents.	Remarks.
Antifriction metal . . .	85.0	—	5.0	Sb 10.0	For bearings. (Ledebur).
Babbitt's metal	69.0	19.0	4.0	Sb 3.0 ; Pb 5.0.	

BISMUTH ALLOYS (FUSIBLE METAL).

—	Bi.	Pb.	Sn.	Cd.	Melting Point.
					° C.
Newton's alloy . .	50.0	31.25	18.75	—	95
Rose's " . .	50.0	28.10	24.64	—	100
Darcet's " . .	50.0	25.00	25.00	—	93
Wood's " . .	50.0	24.00	14.00	12.00	66—71
Lipowitz's " . .	50.0	27.00	13.00	10.00	60

ALLOYS FOR COINAGE.

—	Au.	Cu.	Ag.	Other Constituents.	Remarks.
Gold coin . .	91.66	8.33	—	—	British standard. " Latin Union " and American. Roman, Septimus Severus, 265 A.D.
" . .	90.0	10.0	—	—	
" . .	1.33	82.73	15.93	—	
Silver coin . .	0.1	7.1	92.5	Pb 0.2	Roman, B.C. 31, almost same as British silver coin.
Gold coin . .	40.35	19.63	40.02	—	Early British, B.C. 50.
Silver coin . .	—	7.5	92.5	—	British standard.

CHAPTER IV.

THE THERMAL TREATMENT OF METALS.

Annealing, Hardening, and Tempering.—The mechanical properties of metals are often, in a great measure, dependent on the thermal treatment to which they have been subjected. The effect of heat on zinc has already been noticed. There can be no question that the application of heat to a metal may produce a remarkable molecular change in its structure, the nature of the change depending on that of the metal or alloy, and on the treatment it has undergone. It will be well, therefore, to consider carefully what happens when metals are submitted to the three principal operations involving thermal treatment, which are known respectively as **annealing, hardening, and tempering**. Usually all three are intimately related. Annealing may be defined as the release of strain in metals which may itself have been produced by mechanical treatment, such as hammering, rolling, or wire-drawing, or by either rapid or slow cooling from a more or less elevated temperature. As an example of the former, it may be mentioned that metals and alloys which have been rendered excessively hard by rolling are heated usually to bright redness and allowed to cool slowly. In the case of copper, it does not appear to be important whether the cooling is slow or rapid, and in recent years much experimental evidence has been accumulated, which tends to show that in the case of certain metals which have been hardened, a more or less prolonged exposure to a low temperature under 100° will sensibly anneal them. On the other hand, the rapidity with which the cooling is effected is very important. Bronze containing about 20 per cent. of tin* is rendered very malleable by rapid cooling, and so are certain alloys of iron with more than 7 per cent. of manganese. It is, however, in the case of iron and steel that thermal treatment is especially important.

Steel, it must be remembered, is modified iron. The name iron is, in fact, a comprehensive one, for the mechanical behaviour of the metal is so singularly changed by influences acting from within

* Riche, *Ann. de Chim. et de Phys.*, vol. xxx. (1873), p. 417.

and without its mass as to lead many to think, with Paracelsus, that iron and steel must be two distinct metals, their properties being so different. Pure iron may be prepared in a form pliable and soft as copper, steel can readily be made sufficiently hard to scratch glass; and notwithstanding this extraordinary variance in the physical properties of iron and certain kinds of steel, the chemical difference between them is comparatively very small, and would hardly secure attention if it were not for the importance of the results to which it gives rise. It is necessary to consider the nature of the transformations which iron can sustain, and to see how it differs from steel, of which an old writer has said: "Its most useful and advantageous property is that of becoming extremely hard when ignited and plunged in cold water, the hardness produced being greater in proportion as the steel is hotter and the water colder. The colours which appear on the surface of steel slowly heated direct the artist in *tempering* or reducing the hardness of steel to any determinate standard." There is still so much confusion between the words "temper," "tempering," and "hardening," in the writings of even very eminent authorities, that it is well to keep these old definitions carefully in mind. *Hardening* is the result of rapidly cooling a strongly heated mass of steel. *Tempering* consists in re-heating the hardened steel to a temperature far short of that to which it was raised before hardening; this heating may or may not be followed by rapid cooling. *Annealing*, as applied to steel, consists in heating the mass to a temperature higher than that used for tempering, and allowing it to cool slowly.

This may be shown experimentally in the following manner:—Three strips of steel of identical quality may be taken. It can be shown by bending one that it is soft; but if it is heated to redness and plunged in cold water it will become hard and will break on any attempt to bend it. The second strip may, after heating and rapid cooling, be again heated to about the melting point of lead, when it will bend readily, but will spring back to a straight line when the bending force is removed. The third piece may be softened by being cooled slowly from a bright red heat, and this will bend easily and will remain distorted.

The metal has been singularly altered in its properties by comparatively simple treatment, and all these changes, it must be remembered, have been produced in a solid metal to which nothing has been added, and from which nothing material has been taken.

* *The First Principles of Chemistry*, by W. Nicholson, London, 1760, p. 312.

The theory of the operation, described above, has been laboriously built up, and its consideration introduces many questions of great interest, both in the history of science and in our knowledge of molecular physics.

History.—First, as regards the history of the subject. The knowledge that steel might be hardened must have been derived from remote antiquity. Copper hardened with tin was its only predecessor, and it continued to be used very long after it was known that steel might be hardened. It would, moreover, appear that a desire to appreciate the difficulties of a people, to whom cutting instruments of hard steel were unknown, seems to have induced experimenters in quite recent times to fashion implements of bronze, and a trustworthy authority states that "Sir Francis Chantry formed an alloy containing about 16 parts of copper, $2\frac{1}{2}$ of zinc, and $2\frac{1}{2}$ of tin, of which he had a razor made, and even shaved with it."^{*} The Greek alchemical MSS., which have been so carefully examined by M. Berthelot, give various receipts, from which it is evident that in the early days the nature of the quenching fluid was considered to be all important. There were certain rivers the waters of which were supposed to be specially efficacious. Pliny, who says that the difference between waters of various rivers can be recognised by workers in steel, also knew that oil might be used with advantage for hardening certain varieties of the metal. It is sad to think how many of the old recipes for hardening and tempering have been lost. Theophilus, writing in the eleventh century, gives very quaint instructions in the art of hardening steel. The belief, however, in the efficacy of curious nostrums and solutions for hardening steel could hardly have been firmer in the third century B.C. than in the sixteenth of our era. Pure cold water is now usually employed for hardening, but it was far too simple a material for many a sixteenth-century artificer to employ, as is shown by the quaint recipes contained in one of the earliest books of trade secrets, which, by its title, showed the existence of the belief that the "right use of alchemy" was to bring chemical knowledge to bear upon industry. The earliest edition was published in 1531,[†] and the first English translation ‡ in 1583, from which the following extracts may be of interest. "Take anayles, and first drawn water of a red die of which water being taken.

^{*} *Engines of War*, by H. Wilkinson, 1841, p. 194.

[†] *Rechter Gebrauch d. Alchimei*, 1531. There were many English editions.

[‡] "A profitable booke declaring dyuers approoued remedies, &c., London, 1583. See Prof. Ferguson's learned paper "On some Early Treatises on Technological Chemistry," *Phil. Soc. Glasgow*, Jan. 1886, vol. xvii. p. 206.

in the two first monthes of haruest when it raynes," boil it with the snails, "then heate your iron red hot and quench it therein, and it shall be hard as steele." "Ye may do the like with the blood of a man of xxx years of age and of a sanguine complexion, being of a merry nature and pleasant . . . distilled in the middst of May." This may seem trivial enough, but the belief in the efficacy of such solutions survived into the present century, for in a work published in 1810 the artist is prettily directed* "to take the root of blue lilies, infuse it in wine and quench the steel in it," and the steel will be hard; on the other hand, he is told that if he "takes the juice or water of common beans and quenches iron or steel in it, it will be soft as lead." As must always be the case when the practice of an art is purely empyrical, such procedure was often fantastic, but it is by no means obsolete, for probably at the present day there is hardly a workshop in which some artificer could not be found with a claim to possess a quaint nostrum for hardening steel. Even the use of absurdly compounded baths was supported by theoretical views. Otto Tachen,† for instance, writing of steel in about the year 1666, says that steel when it is "quenched in water acquires strength, because the light alcaly in the water is a true comforter of the light acid in the iron, and cutlers do strengthen it with the alcaly of animals," hence the use of snails. Again, Lemery‡ explains in much the same way the production of steel by heating iron in the presence of horns of animals.

These points have been dwelt upon in order to bring out clearly the fact that the early workers attached great importance to the nature of the fluid in which hot steel was quenched, and they were right, though their theories may have been wrong. The degree of rapidity with which heat is abstracted from the steel during the operation of hardening is as important at the present day as it ever was. Roughly speaking, if steel has to be made glass hard, ice-cold water, brine, or mercury is used; if it has only to be made slightly hard, hot water or oil may be employed; while, as Thomas Gill § suggested in 1818, both "hardening" and "tempering" may be united in a single operation by plunging the hot metal in a bath of molten lead or other suitable metal, which will, of course, abstract the heat more slowly.

The use of lead and of other metals in hardening steel has,

* *The Laboratory; or, School of Arts*, sixth edition, 1739, p. 126. There is a later edition of 1810.

† *Key to the Ancient Hippocratical Learning*, London, 1690, p. 68.

‡ *A Course of Chymistry*, second edition, 1686, p. 131.

§ Thomson's *Annals of Philosophy*, vol. xii. (1818), p. 58.

however, long been known. Réaumur* described in 1722 a method of hardening the points of tools by forcing them when hot into solid tin and lead, and he hints at the use of solid masses of gold, silver, and copper as cooling metals. This old work blends curiously into the new, for the cold metallic surfaces suggested by Clémendot† doubtless play an important part in his process of hardening by compression; whilst another process, that of hardening by water spray, of which much has been heard recently in connection with the manufacture of artillery, is at least a century old.‡ In recent years Jarolimek§ has studied the conditions under which the process may be practised with success, the vaporisation of the liquid appearing to be all-important.

Probably the earliest reference to the use of mercury as a cooling fluid is that made by Réaumur; but in no direction has the modern development of hardening processes been more important than in connection with the use of baths, in which the fluid, being a molten metal, is not readily vaporised. Lisbonne|| has shown what remarkable results as regards resistance to penetration have attended the adoption of the process of hardening armour plates in lead baths, which, as Éverard¶ shows, must be capacious and not heated above the melting point of lead, his experiments leading to the conclusion that armour-plates so quenched in lead are very difficult to penetrate, and present great resistance to fracture.

Internal Constitution of Steel.—The development of theories relating to the internal constitution of steel must now be traced. The advent of the Phlogistic School with the teaching of Becher and Stahl led to the view that iron gained phlogiston during its conversion into steel. By Phlogiston the early chemists really meant *energy*, but to them phlogiston was represented to be a kind of soul possessed by all metals, which they could lose by burning and regain by the process they called “revivication,” “Hardness [in metals] is caused by the jeunenesse of the spirit and their imparity with the tangible parts,” said Francis Bacon;** while, according to Stahl,†† steel was merely iron possessing, in

* *L'art de convertir le fer forgé en acier*, Paris, 1722, p. 351.

† *Comptes Rendus*, vol. xciv. (1882), p. 703.

‡ Guyton de Morveau, *Encyc. Méthodique*, Paris, 1786, p. 436.

§ *Oester. Zeit. für Berg. und Hüttenwesen*, 1876, p. 70.

|| *Génie civil*, vol. xiii. (1888), p. 22.

¶ Paper read at the International Congress of Mining and Metallurgy, Paris, 1889.

** *Sylva Sylvarum*, second edition, 1628, p. 215.

†† *Fundamenta Chemia*, part iii., p. 451, quoted by Guyton de Morveau in the article “Acier,” *Encyc. Méthodique*, p. 421, Paris, 1786.

virtue of its phlogiston, the characteristics of a metal in a higher degree, and this view prevails in the writings of Henckel, Newmann, Cramer, Gellert, Rinman and Macquer. This opinion survived with wonderful persistence, but it did not influence the teaching of Réaumur,* who, in 1722, was the first to suggest a physical theory which has been in any way justified by modern research. He assumed that when steel was heated "sulphurs and salts" were driven out from the molecules, which he represents diagrammatically, into the interstitial space between them. The quenching of the steel and its sudden cooling prevented the sulphurs and salts from returning into the molecules, which were thus firmly cemented by the matter between them, and hard rigid steel was the result. In tempering, the sulphurs and salts partially returned into the molecules, and the metal became proportionately soft. He used the Torricellian vacuum to demonstrate that the hardening of steel is not accompanied by the evolution of gas, and he concluded that "since the hardening of steel is neither due to the intervention of a new substance nor to the expulsion of air, it only remains to seek its cause in the changes occurring in its structure." Notwithstanding this, the Phlogistic School were not daunted, and this leads directly to the work of Torbern Bergman, the great professor at the University of Upsala, who, in 1781, showed† that steel mainly differs from iron by containing about $\frac{2}{10}$ per cent. of plumbago, while iron does not. Read in connection with modern research his work seems wonderfully advanced. He was so forcibly impressed by the fact that the great difference in the mechanical properties of different specimens of iron is due to the presence of small quantities of impurity, and that the properties of iron do not vary, as he says, unless by chance the iron has gathered foreign matter, "*nisi forte peregrinum paullo uberius inhæreat metallum*," in which sentence there is even the dawn of the view that, under the influence of small quantities of foreign matter, iron is, as he calls it, polymorphous, and plays the part of many metals. "*Adeo ut jure dici queat, polymorphum ferrum plurimum simul metallorum vices sustinere*."‡ Unfortunately he confounded the plumbago or carbon he had isolated with phlogiston, as did Rinman in 1782, which was strange, because in 1774 the latter physicist had shown that a drop of nitric acid simply whitens wrought iron, but leaves a black stain on steel. Bergman tenaciously held to the phlogistic

* *L'art de convertir le fer forgé en acier*, Paris, 1722, p. 321 et seq.

† *Opuscula Physica et Chemica*, vol. iii., Upsala, 1783; *De Analysis Ferri*, a dissertation delivered June 9, 1781.

‡ *De Analysis Ferri*, p. 4.

theory in relation to steel; it was inevitable that he should. The true nature of oxidation had been explained; no wonder that the defenders of the phlogistic theory should seek to support their case by appealing to the subtle and obscure changes produced in iron by such apparently slight causes. Bergman's view was, however, combated by Vandermonde, Berthollet and Monge,* who showed in a report communicated to the *Académie des Sciences* in 1786 that the difference between the main varieties of iron is determined by variation in the amount of carbon, and further that steel must contain a certain quantity of carbon in order that it might possess definite qualities. Bergman died in 1784, and the report to which reference has been made is full of respect for "this grand chemist," as its authors call him, "whom science had lost too soon."

Kirwan's essay on Phlogiston,† in which Bergman's views were defended, elicited a reply from Lavoisier himself, and brought down the French school in strength to contest almost the last position occupied by the believers in phlogiston.‡

Bergman's was almost the first calorimetric work, and it is impossible to read it without feeling that in paying the just tribute to Lavoisier's genius Bergman has been overlooked. He desired to ascertain whether pure iron, steel, and cast iron contain the same amount of heat. He therefore attacks the materials with a solvent, and notes the heat evolved. He says the solvent breaks up the assemblage of the aggregation of molecules and forms other unions. If the new body demands more heat than the body which has been disunited then the thermometer falls. If, on the other hand, the degree of heat required is less, the environment will be heated, which will result in the rise of the thermometer. In modern language, when a chemical compound is formed, heat is evolved and energy is lost, but if one substance, say a metal, simply dissolves another, the solution is attended with absorption of heat, and the product when attacked by a suitable solvent should evolve practically the same amount of heat, but certainly not less than would be evolved by the individual metals present in solution.§ This is specially interesting from its relation to the calorimetric work of Lavoisier and Laplace in 1780 and of Lavoisier in 1782, which led him to explain the

* *Histoire de l'Académie Royale des Sciences*, 1786 (printed 1788), p. 132.

† *Essay on Phlogiston and the Constitution of Acids*, 1787, p. 134.

‡ *Essai sur le Phlogistique traduit de l'Anglois de M. Kirwan, avec des Notes de MM. de Morveau, Lavoisier, de la Place, Monge, Berthollet, et de Fourcroy*. Paris, 1788.

§ See French translation of Bergman's work, Paris, 1783, p. 72.

nature of oxidation, and to show that a metal could be as truly calcined or oxidised by the action of a solution as by the action of air at an elevated temperature. Now that the importance of thermal chemistry is beginning to be recognised in relation to industrial chemistry and metallurgy, it is to be hoped that Bergman's merits will be more fully considered. The main point is that he taught that the difference between iron and steel consists in the $\frac{1}{10}$ ths to $1\frac{1}{2}$ per cent. of carbon which steel contains.

It was only natural that Black, writing in 1796, should have attributed the hardening of steel to the "extrication of latent heat," "the abatement of the hardness by the temper" being due, he says, "to the restoration of a part of that heat."* Black failed to see that the work of Bergman had entirely changed the situation. The next step was made in France. It was considered necessary to establish the fact that carbon is really the element which gives steel its characteristic properties, and with this object in view, Clouet,† in 1798, melted a little crucible of iron, weighing 57.8 grammes, containing a diamond, weighing 0.907 gramme, and obtained a fused mass of steel. Fig. 33 shows a plan of the iron crucible and diamond from the drawing in Guyton de Morveau's paper.

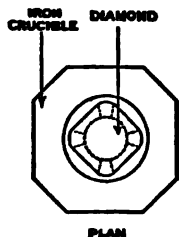


FIG. 33.

His experiment was repeated by many observers, but the results were open to doubt from the fact that furnace gases could always obtain access to the iron and might, as well as the diamond, have yielded carbon to the iron. The carbon might have been presented to the iron in the form of a gas capable of

yielding carbon, and this element would as surely have found its way into the steel.

Margueritte‡, for instance, in 1865, repeated Clouet's experiment, and showed that although carburisation can be effected by simple contact of iron and carbon, it is nevertheless true that in the ordinary process of cementation the gas carbonic oxide plays an important part, which had until then been overlooked. The discovery of Graham,§ in 1866, of the occlusion of carbonic oxide by iron, gave additional support to this theory.

* *Lectures on the Elements of Chemistry*, vol. ii. (1803), p. 505.

† Experiment described by Guyton de Morveau, *Ann. de Chim.*, vol. xxxi. (1799), p. 328.

‡ "Sur l'acétation," *Ann. Chim. et Phys.*, t. vi., 1865, p. 55.

§ *Phil. Trans. Roy. Soc.*, 1866, pp. 399-439.

The question, however, of the direct carburisation of iron by the diamond has never been doubted since 1815, when a working cutler, W. H. Pepys,* heated iron wire and diamond dust together and obtained steel, the heat being afforded by a powerful electric battery. The absorption of carbon in the diamond form by iron may be made clear by reference to the diagram (Fig. 34), which represents a glass vessel, which may either be rendered vacuous or may be filled with an atmosphere of gas through the tube *d*. An iron wire, *b*, placed between the terminals of a battery, *c, c'*, is heated to redness, and remains glowing until it is touched by pure diamond dust, which is effected by raising the cup, *a*. The iron combines with the diamond dust, and fuses.

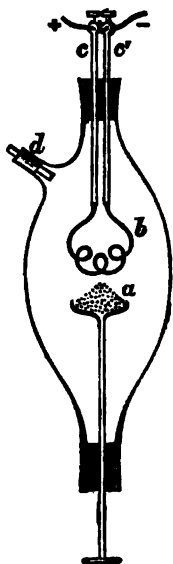


FIG. 34.

It must not be thought, however, that the steel owes its hardness to the passage of diamond into the iron *as diamond*. Margueritte's form of Clouet's experiment may be repeated by using a vacuum instead of an atmosphere of gas, and employing the form of apparatus shown in Fig. 35, which represents an arrangement for heating the diamond and iron *in vacuo*. A strip of pure iron, *b*, is placed between two terminals, *c, c'*, which are connected with a dynamo. The vessel (of glass) is rendered vacuous by connecting the tube *d* with a Sprengel pump. The iron is then heated by the dynamo and maintained

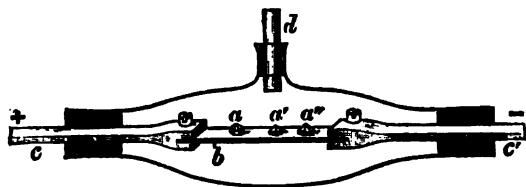


FIG. 35.

glowing until all occluded gas is expelled from the iron, which is then allowed to cool *in vacuo*. Small, pure diamonds, *a, a', a''*, are then placed on the strip of iron through the orifice into which the

* *Phil. Trans. Roy. Soc.*, 1815, p. 371.

tube & fits. The vessel is rendered vacuous, and when the iron is again heated in contact with the diamonds it fuses and combines with them. The diamond by union with iron has passed partially at least to the other form of carbon, graphite; while treatment with a solvent which removes the iron shows that carbon has entered into intimate association with the iron, a fact which leads us to the next step in the study of the relations between carbon and iron.

Hempel* has shown that, in an atmosphere of nitrogen, solid iron appears to assimilate the diamond form of carbon more readily than either the graphitic or the amorphous forms, but directly carbon is associated with *molten* iron it behaves like the protean element it is, and the state which this carbon assumes is influenced by the rate of cooling of the molten mass, or even by the thermal treatment to which the solidified mass is subjected. As carbon is well known to exist in the distinctive forms of diamond, graphite, and soot, it need not be considered strange that carbon should be capable of being present in intimate association with iron, but in very varied forms.

The mode of existence of carbon in soft annealed steel is very different from that in which it occurs in hard steel. Karsten was the first to isolate, in 1827, from soft steel a true compound of iron and carbon; Berthier† also separated from soft steel a carbide of iron to which he assigned the formula Fe_3C ; and it need only be added that within the last few years Sir F. Abel‡ has given much experimental evidence in favour of the existence in soft cold-rolled steel of a carbide, Fe_3C , which he isolated by the slow solvent action of a chromic acid solution. His work has been generally accepted as conclusive, and has been the starting-point of much that has followed.

Obviously the microscope should reveal wide differences between the structure of various kinds of iron and steel; and Sorby, in his very delicate investigations into the structure of steel,§ has shown that this is the case; the point of main importance being the existence of a substance which Sorby called the "pearly constituent" in soft steel. This pearly constituent is closely related to the carbide of iron, Fe_3C , of Abel, and is probably a mixture of Fe_3C and pure iron. Its presence is diagrammatically indicated in Fig. 36. The diagram will serve for the purpose of illustration to indicate the appearance when soft,

* *Ber. der deutsch. chem. Gesellschaft*, vol. xviii. (1885) p. 998.

† *Ann. des Mines*, vol. iii. (1833), p. 229.

‡ *Proc. Inst. Mech. Eng.*, 1883, p. 56.

§ *Journ. Iron and Steel Inst.*, No. 1 (1887), p. 255.

hardened, and tempered steel are respectively heated with a solvent which acts gently on the mass.

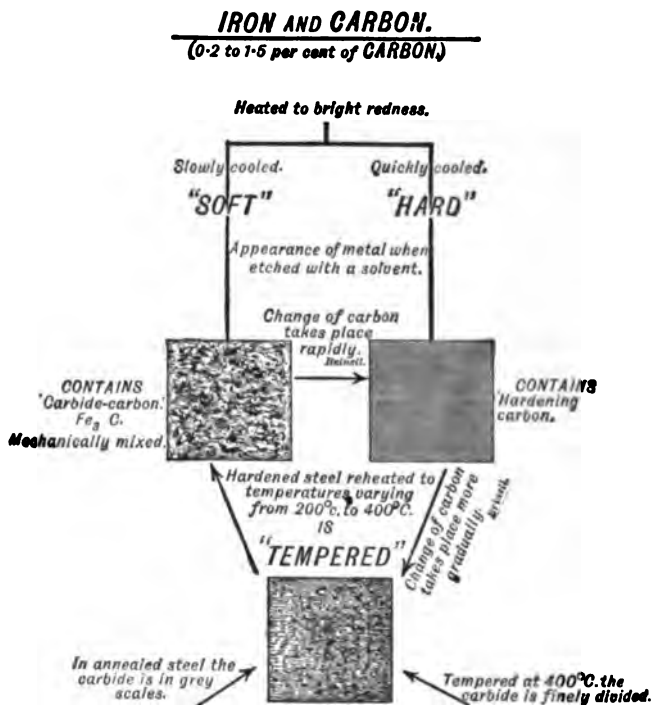


FIG. 36.

A study of the admirable work of Ledebur* will show how complex the relations of carbon and iron really are, but the question arises, Does a change in the "mode of existence" of carbon in iron sufficiently explain the main facts of hardening and tempering? It does not. It is possible to obtain by rapid cooling from a certain temperature steel which is perfectly soft, although analysis proves that the carbon is present in the form which has been recognised as "hardening carbon." No doubt in the hardening of steel the carbon changes its mode of existence;

* *Stahl und Eisen*, vol. viii. (1888), p. 742; and *Journ. Iron and Steel Inst.*, 1893. Part II.

but some other theory must be sought which will explain all the facts, and in order to do this it is necessary to turn to the behaviour of the iron itself.

In approaching this portion of the subject, a few elementary facts relative to the constitution of matter must be recalled, and in doing so a brief appeal to history must again be made. It is universally accepted that metals, like all elements, are composed of atoms of definite weights and volumes grouped in molecules. In order actually to transmute one metal into another it would be necessary to discover a method of attacking, not the molecule, but the *atom*, and of changing it, and this, so far as is known, has not yet been done; but it is possible, by influences which often appear to be very slight, to change the relations of the molecules to each other, and to alter the arrangement or distribution of the *atoms* within the *molecules*, and by varying, in this sense, the molecular arrangement of certain elements, they may be made to pass into states which are very different from those in which we ordinarily know them. Carbon, for instance, when free, or when associated with iron, may readily be changed from its diamond form to the graphitic state, though the converse change has not as yet been effected.

Sulphur, again, best known as a hard, brittle, yellow solid, may be prepared and maintained for a little time in the form of a brown viscous mass, but this latter form of sulphur soon passes spontaneously and slowly at the ordinary temperature, and instantaneously at 100° , to the solid octahedral yellow modification with evolution of heat. The viscous form of sulphur is an allotropic modification of that element. A few cases of allotropy in metals have already been described in Chapter III., and when they do occur they give rise to problems of vast industrial importance. Such molecular changes in metals are usually produced by the addition of a small quantity of foreign matter, and it would appear that the molecular change produced by the action of *traces* upon *masses* is a widespread principle of nature, and one which was recognised at the dawn of the science of chemistry, even in the seventh century, but distorted explanations were given of well-known facts, and gave rise to entirely false hopes. But students would do well to bear in mind that it is the same story now as in mediæval times; the single grain of powder which Raymond Lully said would transmute millions of its weight of lead into gold, the single grain of stone that Solomon Trismosin thought would secure perpetual youth, had their analogues in the small amount of plumbago which to Bergman's astonishment in the eighteenth century converted

iron into steel. By his time it was recognised that the right use of alchemy consisted in the application of its methods to industry, and we still wonder at the minuteness of the quantity of certain elements which can profoundly affect the properties of metals. The statements are true, and are not derived from poetical literature early or late. There is no need to fear the taunt of Francis Bacon,* that "sottishly do the chymics appropriate the fancies and delights of poets in the transformation of bodies to the experiments of their furnaces," for, although it may not be possible to *transmute* metals, it is easy so to *transform* them by very slight influences, that as regards special service required from them they may behave either usefully or entirely prejudicially.

The question at once suggests itself, Can iron behave in a similar manner; is an allotropic form of iron known? Joule afforded experimental evidence for an affirmative answer to this question many years ago, by communicating to the British Association in 1850 a paper on some amalgams. The result of his experiments, published in detail later,† in a paper which has been sadly neglected, showed that iron released from its amalgam with mercury is chemically active, as it combines readily with the oxygen of the air at the ordinary temperature, and he claims that the iron so set free is allotropic; but Joule did much more than this. Magnus had shown (1851) that the thermo-electric properties of hard and of soft steel and iron differ. Joule, in a paper on some thermo-electric properties of solids, incidentally shows that the generation of a thermo-electric current affords a method of ascertaining the degree of carburisation of iron, and he appeals to the "thermo-electricity of iron in different states" as presenting a "fresh illustration of the extraordinary physical changes produced in iron by its conversion into steel," and he adds the expression of the belief "that the excellence of the latter metal might be tested by ascertaining the amount of change in thermo-electric condition which can be produced by the process of hardening."‡ It is by a thermo-electric method that the views as to the existence of iron in allotropic forms have been confirmed.

Jullien seems to have inclined to the view that iron is allotropic in his *théorie de la trempe*,§ published in 1865, but he

* Preface to the *Wisdom of the Ancients*.

† "On Some Amalgams," *Mem. Lit. Phil. Soc. Manchester*, vol. II. [3], p. 115.

‡ *Phil. Trans.*, vol. cxlix. (1859), p. 95.

§ *Annexe au Traité de la Métallurgie du Fer*, 1865.

cannot be said to have done much beyond directing attention to the importance of hardening and tempering steel.

The next step was made in Russia, in 1868. Chernoff showed that steel could not be hardened by rapid cooling until it had been heated to a definite temperature, to a degree of redness which he called *a*. Then, in 1873, Professor Tait* used this expression in a Rede Lecture delivered at Cambridge: "It seems as if iron becomes, as it were, a different metal on being raised above a certain temperature; this may possibly have some connection with the ferricum and ferrosium of the chemists." He also published his now well-known "first approximation to a thermo-electric diagram," which is of great interest in view of recent work. At about this time those specially interested in this question remembered that Gore† had shown that a curious molecular change could be produced by heating an iron wire. Barrett repeated Gore's experiment, and discovered that as an iron wire cools down it suddenly *glows*, a phenomenon to which he gave the name *recalcescence*, and these investigations have been pursued and developed in other directions by many skilful experimenters.‡ In 1879 Wrightson called attention to the abnormal expansion of carburised iron at high temperatures.

The next point of special importance appears to be that recorded by Barus, who, by a thermo-electric method, showed, in an elaborate paper published in 1879,§ that "the hardness of steel does not increase continuously with its temperature at the moment of sudden cooling, but at a point lying in the dark-red heat state" may suddenly be attained by rapid cooling. Brief reference will again be made to the remarkable series of papers published by Barus and Strouhal,|| embodying the results of

* *Nature*, vol. viii. (1873), pp. 86, 122, and *Trans. Roy. Soc. Edin.*, vol. xxvii. (1873), p. 125.

† Gore, *Proc. Roy. Soc.*, vol. xvii. (1869), p. 260. Barrett, *Phil. Mag.*, vol. xli. (1873), p. 472.

‡ G. Forbes, *Proc. Roy. Soc. Edin.*, vol. viii. (1874), p. 363. Norris, *Proc. Roy. Soc.*, vol. xxvi. (1877), p. 127. Tomlinson, *Phil. Mag.*, vol. xxiv. (1887), p. 256; vol. xxv. (1888), pp. 45, 103, and 372; vol. xxvi. (1888), p. 18. Newall, *ibid.*, vol. xxiv. (1887), p. 435; vol. xxv. (1888), p. 510.

§ Barus, *Phil. Mag.*, vol. viii. (1879), p. 341.

|| Hardness (temper), its electrical and other characteristics: Barus, *Phil. Mag.*, vol. viii. (1879), p. 341; *Wied. Ann.*, vol. vii. (1879), p. 383; Strouhal and Barus, *ibid.*, vol. xi. (1880), p. 930; *ibid.*, vol. xx. (1883), p. 525. Hardness and magnetisation, *ibid.*, vol. xx. (1883), pp. 537, 662. Density and (internal) structure of hard steel and of quenched glass, Barus and Strouhal, *American Journ.*, vol. xxxi. (1886), p. 386; *ibid.*, p. 439; *ibid.*, p. 181. Temper and chemical composition, *ibid.*, vol. xxxii. (1886), p. 276. Temper and viscosity, *ibid.*, p. 444; *ibid.*, vol. xxxiii. (1887), p. 20; Barus *ibid.*, vol. xxxiv. (1887), p. 1; *ibid.*, p. 175. These papers, systemati

laborious investigations, to which but scanty justice can be done here; and finally within the last few years Pionchon* showed that at a temperature of 700° the specific heat of iron is altogether exceptional, and Le Chatelier† has detected that at 700° a change occurs in the curve representing the electromotive force of iron, both experimenters concluding that they had obtained evidence of the passage of iron into an allotropic state. Osmond,‡ in France, then made the observations of Gore and Barrett the starting-point of a fresh inquiry. Bearing in mind the fact that molecular change in a body is always accompanied with evolution or absorption of heat, which is, indeed, the surest indication of the occurrence of molecular change, he studied, with the aid of a chronograph, what takes place during the slow cooling and the slow heating of masses of iron or steel, using as a thermometer to measure the temperature of the mass a thermo-electric couple of platinum, and of platinum containing 10 per cent. of rhodium, converting the indications of the galvanometer into temperatures by Tait's formulæ.

Figs. 37 and 38 show the actual mode of conducting the experiments. F, Fig. 37, is a piece of steel into which a platinum and



FIG. 37.

platinum-rhodium couple, t, t' , is fixed. It is enclosed in a glazed porcelain tube, and heated to bright redness in the furnace S (Fig. 38). This tube, T, may be filled with any gaseous atmosphere. C is a bulb filled with chloride of calcium. The metal under examination is slowly cooled down. The wires from the thermo-couple pass to the galvanometer, G. The rate of cooling of the mass, as indicated by the movement of a spot of light from the

cally discussed and enlarged, are embodied with new matter in the *Bulletins of the United States Geological Survey*—viz., *Bull.* No. 14 (1885), pp. 1-226; *Bull.* No. 27 (1886), pp. 30-61; *Bull.* No. 35 (1886), pp. 11-60; *Bull.* No. 42 (1887), pp. 98-131.

* *Comptes Rendus*, vol. cii. (1886), pp. 675 et 1454; vol. ciii. (1886), pp. 743 et 1135.

† *Ibid.*, vol. cii. p. 819.

‡ The reader will find the principal part of Osmond's work in the following papers:—Osmond et Werth, *Théorie cellulaire des Propriétés de l'Acier*, *Ann. des Mines*, vol. viii. (1885), p. 5; *Transformations du Fer et du Carbone*, Paris, Baudouin et Cie., 1888; *Études métallurgiques*, *Ann. des Mines*, Juillet-Août, 1888. There is also a very interesting paper, *Sur les nouveaux Procédés de Trempe*, which he communicated to the Mining and Metallurgical Congress, Paris, 1889, and another in the *Journ. Iron and Steel Inst.*, No. 1 (1890), p. 38.

galvanometer mirror, M, on the screen, R, is recorded by a chronograph. The source of light is shown at L.

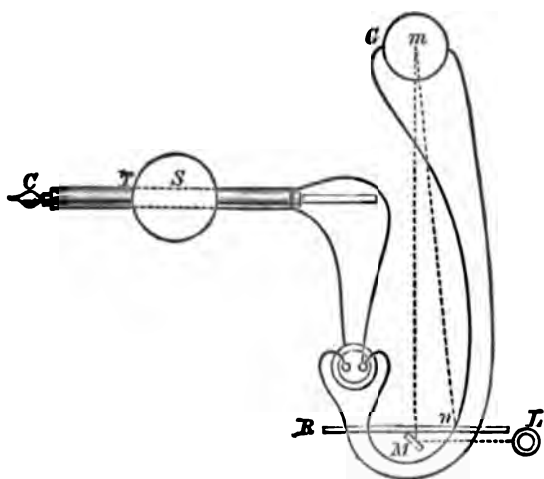


FIG. 38.

The curves given in the diagram, Fig. 39, show how the rate of movement of the spot of light varies with different samples of steel. The stoppage of the movement of the spot of light of course indicates the evolution of heat from the cooling mass of steel, F (Fig. 37).

It will be seen, therefore, that although the presence of carbon is essential to the hardening of steel, it need not, as has hitherto been supposed, change its mode of existence when soft steel is hardened. (See p. 126.)

In Fig. 39 the temperatures through which a slowly cooling mass of iron or steel passes are arranged along the horizontal line, and the intervals of time during which the mass falls through a definite number (6.6) of degrees of temperature are shown vertically by ordinates. See what happens while a mass of electro-deposited iron (shown by a dotted line), which is as pure as any iron can be, slowly cools down. From 1200° to 870° it falls uniformly at the rate of about 2.2° a second, and the intervals of temperature are plotted as dots at the middle of the successive points of the intervals. When the temperature falls down to 858° there is a sudden arrest in the fall of temperature; the indicating spot of light, instead of falling at a uniform rate of about

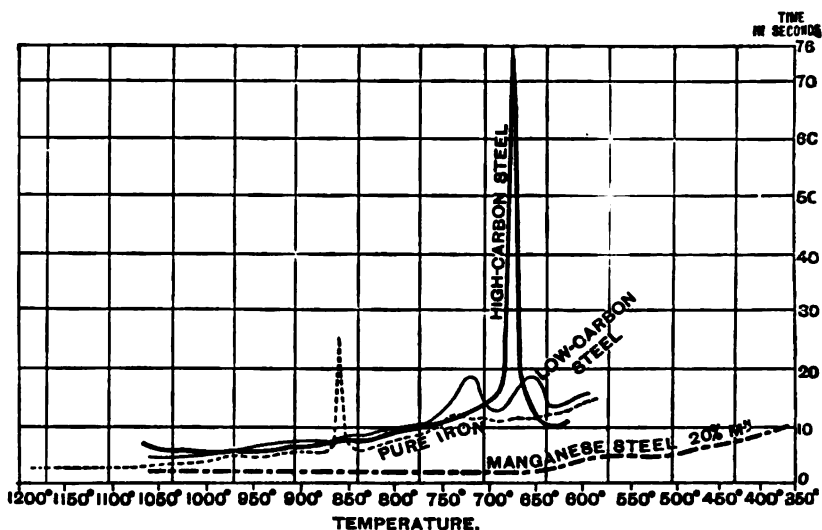


FIG. 39

2° a second, suddenly takes 26 seconds to fall through an interval of temperature which hitherto and subsequently only occupies about 6 seconds. The diagram (Fig. 39) shows what actually happens when the iron contains carbon in the proportion required to constitute it mild steel (indicated by a thin continuous line, Fig. 39), there is not one, but there are two such breaks in the cooling, and both breaks occur at a different temperature from that at which the break in pure iron occurred. As the proportion of carbon increases in steel the first break in cooling travels more and more to the right and gradually becomes confounded with the second break, which, in steel containing much carbon, is of long duration, lasting as much as 76 seconds in the case of steel containing 1.25 per cent. of carbon (thick continuous line, Fig. 39).

Now, it may be urged, as the presence of carbon has evidently an influence on the cooling of steel when left to itself, may it not affect molecular behaviour during the rapid cooling which is essential to the operation of hardening? It is known that the carbon during rapid cooling passes from the state in which it is combined with the iron into a state in which it is dissolved in the iron; it is also known that during slow cooling this dissolved

carbon can re-enter into combination with the iron so as to assume the form in which it occurs in soft steel. Osmond claims that this second arrestation in the fall of the temperature corresponds to the recalescence of Barrett, and is caused by the reheating of the wire by the heat evolved when carbon leaves its state of solution and truly combines with the iron.

If it is hoped to *harden* steel it must clearly be rapidly cooled before this combination of carbon and iron has taken place, or it will be too late to keep the carbon as hardening carbon. But what does the first break in the curves mean? It will be seen that it occurs in electrolytic iron, which is free from carbon; it must, then, indicate some molecular change in iron itself, accompanied with evolution of heat, a change with which carbon has nothing whatever to do, for no carbon is present, and Osmond argues thus:—There are two kinds of *iron*, the atoms of which are respectively arranged in the molecules so as to constitute *hard* and *soft iron*, quite apart from the presence or absence of carbon. In red-hot iron the mass may be soft, but the molecules are hard: let this be called β iron; cool such red-hot pure iron, whether quickly or slowly, and it becomes soft; it passes to the α soft modification, there is nothing to prevent its doing so. It appears, however, that if carbon is present, and the metal be rapidly cooled, the following result is obtained:—A certain proportion of the molecules are retained in the form in which they existed at a high temperature in the hard form, the β modification, and hard

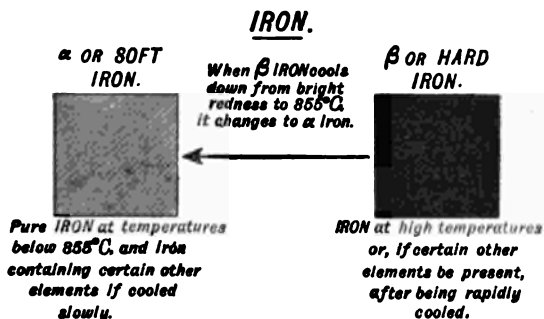


FIG. 40.

steel is the result. The main facts of the case may, perhaps, be made clearer by the aid of the diagram Fig. 40, which shows the relation between α and β iron. This molecular change from β

iron to α iron during the slow cooling of a mass of iron or steel is, according to Osmond's theory, indicated by the first break in the curve representing the slow cooling of iron, as is proved by the fact that it occurs alone in electro-iron. A second break, usually one of much longer duration, marks the point at which carbon itself changes from the dissolved or hardening carbon to the combined, carbide-carbon. It follows that if steel be quickly cooled *after the change from β to α* has taken place, but before the carbon has altered its state—that is, before the change indicated by the second break in the curve has been reached—then the iron should be soft, but the carbon, hardening carbon, and, as such, the action of a solvent should show that it cannot be released from iron in the black carbide form. This proves to be the case, and affords strong incidental proof of the correctness of the view that two modifications of iron can exist.

It will be seen, therefore, that, although the presence of carbon is essential to the hardening of steel, the change in the mode of existence of the carbon is less important than has hitherto been supposed. The α modification of iron may be converted into the β form by stress applied to the metal at temperatures below a dull red heat, provided the stress produces permanent deformation of the iron.*

From the engineer's point of view the most interesting information which the pyrometer (described on p. 151) has as yet afforded is connected with the measurement of internal stresses in iron and steel. It is evident that the occurrence of molecular changes must be of vital importance when the metal is subjected at high temperatures to mechanical operations such as rolling or forging. The question naturally arises, Do the molecular changes in the iron take place at one moment throughout the mass of metal?—that is, is the rate of cooling approximately uniform throughout the mass? Or does the external portion of a hot ingot cool so much more rapidly than the centre as to allow the molecular changes in the iron, and the alterations in the relation between the carbon and the iron, to become complete near the surface long before they take place in the interior of the mass? The experimental difficulties in the way of obtaining information upon these points have hitherto appeared to be insuperable; but the pyrometric method used in this research affords most important evidence, as a brief description of the following experiments will show.

If the steel be allowed to cool under pressure (the student must consult the original memoir† to see how this was effected),

* Osmond, *Études Métallurgiques*, 1888, p. 6. See also Charpy, *Comp. Rend.*, vol cxvii. (1893), p. 850.

† *Inst. Mech. Eng.*, part ii., 1893, p. 125.

it will be found that the point of recalescence is lowered, as will be seen by reference to the curves (Fig. 40a).

The sample of steel contained 0.9 per cent. of carbon, and when cooled in air without pressure recalescence took place at close

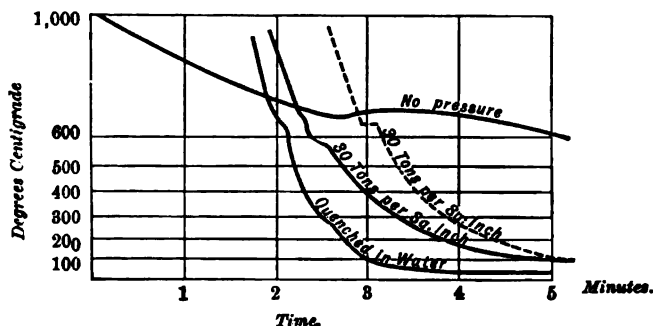


FIG. 40a.

upon 660°. In two experiments shown, respectively dotted and continuous lines marked "30 tons per square inch," the point of recalescence was sensibly lowered by that amount of pressure. When the ingot was quenched in water the recalescence point fell to 300°.

Barus* has pointed out that since most metals can be similarly hardened by straining, it would follow that there should be α and β varieties in all cases, even though a molecular change corresponding to recalescence has only been observed in the case of a few metals. He believes, however, that there is reason to be urged in favour of this extreme view. The existence of mole-

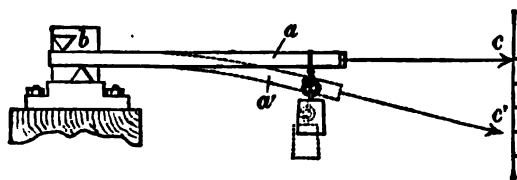


FIG. 41.

cular change in iron may be illustrated by the following experiment:—Take a bar of steel (Fig. 41), containing much carbon. In such a variety of steel, the molecular change of the iron itself, and the change in the relations between the carbon and the iron,

* *Nature*, vol. xli. (1890), p. 369.

would occur at nearly the same moment. Heat this bar to redness, one end of the red-hot bar being firmly fixed (Fig. 41), and sling a weight *not sufficient to bend it* to the free end, which is lengthened by the addition of a reed to magnify any motion that may take place. As the bar is red hot, it ought to be at its softest when it is freshly withdrawn from the furnace, and, if the weight was ever to have power to bend it, it would be then; but, in spite of the rapidity with which such a thin bar cools down in the air and becomes rigid, points of molecular weakness come when the iron changes from β to α , and the carbon passes from hardening carbon to carbide carbon; at that moment, at a temperature much below that at which it is withdrawn from the furnace, the bar will begin to bend. It has been found experimentally that this is the point at which, according to Osmond's theory, molecular change takes place. Coffin takes advantage of this fact to straighten distorted steel axles.*

Barus† traces the connection of this singular minimum of the viscosity of hot iron and the interpretation given of Maxwell's theory of viscosity, and he points out that "when iron passes through the temperature of recalescence, its molecular condition is for an instant almost chaotic. This has now been abundantly proved by Hopkinson. The number of unstable configurations, or, more clearly, the number of configurations made unstable because they are built up of disintegrating molecules, is therefore at a maximum. It follows that the viscosity of the metal must pass through a minimum. Physically considered, the case is entirely analogous to that of a glass-hard steel rod suddenly exposed to 300°. If all the molecules passed from Osmond's β state to his α state together, the iron or steel would necessarily be liquid. This extreme possibility is, however, at variance with the well-known principles of chemical kinetics. The ratio of stable to unstable configurations cannot at any instant be zero. Hence the minimum viscosity in question, however relatively low, may yet be large in value as compared with the liquid state."

Dr. Anderson has recently urged that, "when, by the agency of heat, molecular motion is raised to a pitch at which incipient fluidity is obtained, the particles of two pieces brought into contact will interpenetrate or diffuse into each other, the two pieces will unite into a homogeneous whole, and we can thus grasp the full meaning of the operation known as 'welding.'" It is, however, possible to obtain evidence of interchange of molecular motion, as has been so abundantly shown by Spring,

* *Trans. American Soc. Civil Engineers*, vol. xvi. (1887), p. 324.

† *Nature*, vol. xli. (1890), p. 369.

even at the ordinary temperature, while in the case of steel it must take place far below incipient fluidity, indeed, at a comparatively low temperature, as is shown by the following experiment on the welding of steel. Every smith knows how difficult it is to weld highly carburised hard tool steel, but if the ends of a newly fractured $\frac{1}{2}$ inch square steel rod, *a* (Fig. 42), are covered with platinum foil, *b*, so as to exclude the air, and if the junction is heated in the flame of a Bunsen burner, *c*, the metal will weld, without pressure, so firmly that it is difficult to break it with the fingers, although the steel has not attained a red heat.*

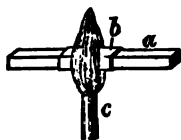


FIG. 42.

The question now arises, what is the effect of the presence of other metals in steel, of which much has been heard recently? Take the case of manganese. This metal enables steel to harden very energetically, as is very well known. If much of it be present, 12 to 20 per cent., in iron, *no break whatever* is observed in the curve which represents slow cooling. (See line marked "Manganese Steel," Fig. 39.) That is, the iron never shows such a change as that which occurs in other cooling masses of iron. Then such a material should be hard, however it is cooled. So it is. There is one other important point of evidence as to molecular change connected with the addition of manganese. Red-hot iron is not magnetic, and Hopkinson† has recently stated that the temperature of recalescence is that at which iron ceases to be magnetic. It may be urged that β iron cannot therefore be magnetised. Steel containing much manganese cannot be magnetised, and it is therefore fair to assume that the iron present is in the β form. Hadfield‡ has given metallurgists wonderful alloys of iron and manganese in proportions varying from 7 to 20 per cent. of manganese. Professor Ewing and others have specially examined the magnetic properties of this material, and Ewing concludes that "no magnetising force to which the metal is likely to be subjected, in any of its practical applications, would produce more than the most infinitesimal degree of magnetisation" in Hadfield's manganese steel. It has been seen that quantities of manganese above 7 per cent. appear to prevent the passage of β iron into the α form. In smaller quantities, manganese seems merely to retard the conversion, and to bring the two loops of the diagram nearer together. With regard to the effect of other elements on

* *Trans. American Soc. Mechanical Engineers*, vol. ix. (1888), p. 155.

† *Proc. Roy. Soc.*, vol. xlv. (1889), pp. 318, 455, and 457.

‡ *Proc. Inst. Civil Engineers*, vol. xciii., 1888, part iii., p. 1.

steel, it need only be added that tungsten possesses the same property as manganese, but in a more marked degree. Chromium has exactly the reverse effect, as it enables the change of hard β iron to soft α iron to take place at a higher temperature than would otherwise be the case, and this may explain the extreme hardness of chromium steels when hardened in the same way as ordinary steels.

The disappearance of the magnetic properties of iron on heating is of much interest in relation to the allotropism of the metal. Gilbert appears to have been the first to demonstrate, in his treatise *de Magnete*, published in 1600, that red-hot iron is not magnetic; and nearly half a century later Sir Thomas Browne,* with frequent reference to Gilbert's work, states that masses of iron, "by the fire, omit whatsoever they had received from the earth or loadstone," and he gives evidence of being aware that what is now called the "magnetic permeability" of iron and steel is affected by heating and cooling the metal. These facts have been recognised as being of vital importance in modern research, and they derive new interest from the sharp identification of the loss of magnetism with the temperature at which a molecular change in the iron takes place, and from Hopkinson's recent discovery that an alloy of iron with 25 per cent. of nickel is magnetisable if it be previously cooled (by solid carbonic anhydride) to a very low temperature.

Working of Steel.—There are a few considerations relative to the actual working of steel which can but briefly be dealt with, notwithstanding their industrial importance. The points *a* and *b* adopted in the celebrated memoir of Chernoff, to which reference has already been made, change in position with the degree of carburisation of the metal. It is useless to attempt to harden steel by rapid cooling if it has fallen in temperature below the point (in the red) *a*, and this is the point of "recalescence" at which the carbon combines with the iron to form carbide carbon; it is called *V* by Brinell. In highly carburised steel, it corresponds exactly with the point at which Osmond considers that iron, in cooling slowly, passes from the β to the α modification. Now with regard to the point *b* of Chernoff (or *W* of Brinell). If steel be heated to a temperature above *a*, but below *b*, it remains fine grained, however slowly it is cooled. If the steel be heated above *b*, and cooled, it assumes a crystalline granular structure, whatever the rate of cooling may

* *Pseudodoxia Epidemica: or Enquiries into Vulgar Errors.* Second Edition, 1650, p. 45.

be. The size of the crystals, however, increases with the temperature to which the steel has been raised.

Now the crystalline structure, which is unfavourable to the steel from the point of view of its industrial use, may be broken up by the mechanical work of forging the hot mass; and the in-

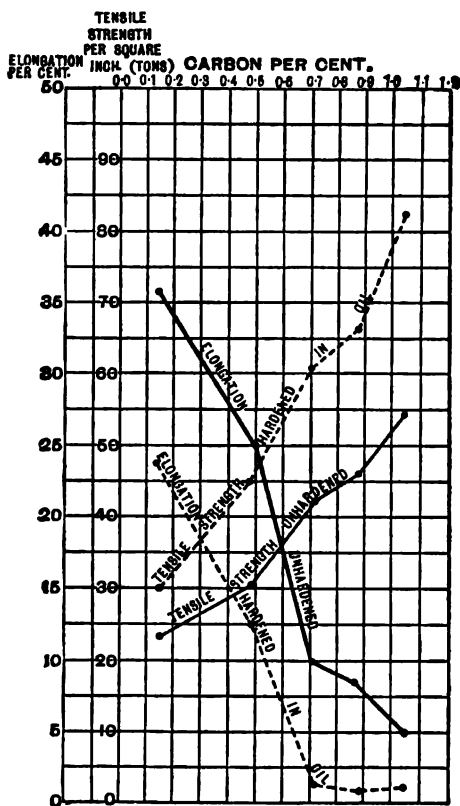


FIG. 43.

vestigations of Abel, of Maitland, and of Noble, have shown how important "work" on the metal is. When small masses of hot steel are quenched in oil, they are hardened just as they would be if water were used as a cooling fluid. The diagram, Fig. 43, shows the way in which the tenacity of steel containing varying

amounts of carbon is increased by oil-hardening,* while at the same time the elongation rapidly diminishes. With large masses the effect of quenching in oil is different. Such cooling of large hot masses appears to break up this crystalline structure in a manner analogous to mechanical working. If the mass of metal is very large, such as a propeller shaft, or tube of a large gun, the change in the relations between the carbon and the iron, or true "hardening" produced by such oil treatment is only effected *superficially*, that is, the hardened layer does not penetrate to any considerable depth, but the innermost parts are cooled more quickly than they otherwise would have been, and the development of the crystals, which would have assumed serious proportions during slow cooling, is arrested. It depends on the size of the quenched mass whether the tenacity of the metal is or is not increased, but its power of being elongated is considerably augmented. This prevention of crystallisation probably constitutes the great merit of oil quenching, which, as regards large masses of metal, is certainly not a true hardening process.

There has been much divergence of view as to the relative advantages of work on the metal and of oil-hardening, but it will be possible to reconcile these views if the facts so briefly stated be considered.

The effect of annealing remains to be dealt with. In a very complicated steel casting, the cast metal probably contains much of its carbon as hardening carbon, and the mass, which has necessarily been poured into the mould at a high temperature, is crystalline. The effect of annealing is to permit the carbon to pass from the "hardening" to the "carbide" form, and, incidentally, to break up the crystalline structure, and to enable it to become minutely crystalline. The result is that the annealed casting is far stronger and more extensible than the original casting. The carbide carbon is probably interspersed in the iron in a finely divided state, and not in crystalline pallets. It would obviously be impossible to "work"—that is, to hammer—complicated castings, and the extreme importance of obtaining a fine crystalline structure by annealing, with the strength which results from such a structure, has been abundantly demonstrated by Mr. J. W. Spencer, of Newcastle.

The effect of annealing and tempering is, in fact, very complicated, as is shown by the long series of researches which Barus and Strouhal have conducted in recent years. They consider that annealing is demonstrably accompanied by chemical change

* This was well shown in Prof. Akerman's celebrated paper on "Hardening Iron and Steel," *Journ. Iron and Steel Institute*, 1879, part ii. p. 504.

even at temperatures slightly above the mean atmospheric temperature, and that the "molecular configuration of glass-hard steel is always in a state of incipient change . . . a part of which change must be of a permanent kind." Barus says "that during the small interval of time within which appreciable annealing occurs, a glass-hard steel rod suddenly heated to 300° is almost a viscous fluid,"* and he considers that glass-hard steel is constantly being spontaneously "tempered" at the ordinary temperature, which he says, "acting on freshly quenched [that is, hardened] steel for a period of years, produces a diminution of hardness about equal to that of 100° C. acting for a period of hours."

The nature of the molecular change is well indicated in the long series of researches which led them to conclude that in steel "there is a limited interchange of atoms between molecules under stress, which must be a property common to solids if, according to Clerk-Maxwell's conception, solids are made up of configurations in all degrees of molecular stability."

Barus and Strouhal attach but little importance to the change in the relations between the carbon and the iron during the tempering and annealing of hard steel. They consider that in hardening steel the "strain once applied to steel is locked up in the metal in virtue of its viscosity"; tempering is the release of this molecular strain by heat.

Highly carburised steels harden very energetically by very slight modifications in thermal treatment, and it will be evident that a very hard material is unsuitable for industrial use if the conditions of its employment are such as to render it desirable that the material should stretch.

To turn to the class of steel which does not harden, it is certain that, although wrought iron passes almost insensibly into steel, there can be no question that, not merely the structural, but the molecular aggregation of even steel containing only $\frac{1}{100}$ per cent. of carbon, is profoundly different from that of wrought iron. The class of steel which was formerly employed for weapons and tools belonged to the highly carburised, readily hardening class. It was the "mild steel," containing but little carbon, which was destined to replace wrought iron, and when attempts were made to effect the general substitution of steel for iron, fears as to its character and trustworthiness unfortunately soon arose, so that from about the year 1860 until 1877, steel was viewed with suspicion. This can now be explained. Doubts as to the fidelity of steel, even when it was obtained free from

* *Phil. Mag.*, vol. xxvi. (1888), p. 209.

entangled cinder, arose from ignorance of the fact that, on either side of a comparatively narrow thermal boundary, iron in steel can practically exist in two distinct modifications. The steel was "true" enough, but, from the point of view of the special duties to be entrusted to it, its fidelity depended on which modification of iron had to be called to the front. Artificers attempted to forge steel after it had cooled down below the point α of Chernoff at which recalescence occurs, and they often attempted to work highly carburised steel at temperatures which were not sufficiently low.

Classification of Steel.—From the foregoing remarks, it will be evident that the use of steel depends almost entirely upon its power of being hardened and tempered. It may not be out of place, therefore, to indicate the way in which steel may be classified from the point of view of its industrial use, according to the amount of carbon it contains. Steels may be grouped under certain definite percentages of carbon, ranging from $\frac{2}{100}$ to $1\frac{1}{2}$ per cent. Each class merges into the other, but the members at either end of the series vary very greatly. It would be impossible to make from boiler plate a razor which would cut, and, conversely, a boiler made of razor steel would possibly fracture at once if it were overheated and subjected to any sudden pressure of steam.

Speaking generally, if the steel contains, in addition to carbon, $\frac{5}{100}$ per cent. of manganese, each class of steel would be equivalent, as regards tenacity and hardening properties, to the one above it.

The steel used for naval construction contains 0.15 to 0.2 per cent. of carbon. And when steel faces are used for the armour plates, the material contains 0.7 to 0.8 per cent. of carbon.

It may be mentioned that a moderate-sized battle ship weighs, fully equipped, about 10,000 tons, there being 3400 tons of steel in the hull, apart from her armour, which, with its backing, will weigh 2800 tons. Later types weigh 14,900 tons.

With regard to steel used in civil engineering, the most remarkable case is presented by the Forth Bridge. The steel of which the compression members of the structure are composed contains 0.23 per cent. of carbon and 0.69 per cent. of manganese. The parts subjected to extension do not contain more than 0.19 per cent. of carbon.*

Steel for the manufacture of pens contains about 0.3 per cent. of carbon. Steel rails contain from 0.3 to 0.4 per cent. of carbon, and in this class slight variations in the amount of carbon are of

* *Journ. Iron and Steel Institute*, vol. ii. (1888), p. 94.

vital importance, as in certain climates a variation of 0.1 per cent. in the amount of carbon may be very serious. The great benefit which has accrued to the country from the substitution of more durable steel rails for the old wrought-iron ones may be gathered from the statement of Webb, of Crewe, which shows that "the quantity of steel removed from the rails throughout the London and North-Western system by wear and oxidation is about 15 cwts. an hour, or 18 tons a day."

Gun steel contains 0.3 to 0.5 per cent. of carbon, and it may contain 0.8 per cent. of manganese. It is in relation to gun steel that oil-hardening becomes very important. The oil tank of the Saint-Chamond Works (on the Loire) is 72 feet deep, and contains 44,000 gallons of oil, which is kept in circulation by rotary pumps, to prevent the oil being unduly heated locally when the heated mass of steel is plunged into it.

Now with regard to projectiles. The most formidable projectiles belong to the highly carburised class of steel. Shells contain 0.8 to 0.94 per cent. of carbon, and, in addition, some of these have 0.94 to 2 per cent. of chromium. The firm of Holtzer showed in the Paris Exhibition a shell which pierced a steel plate 10 inches thick, and was found, nearly 800 yards from the plate, entire and without flaw, its point alone being slightly distorted. Compound armour plate with steel face, containing 0.8 per cent. of carbon, is more difficult to pierce than a simple plate, and armour plate now often contains nickel.

Lastly, reference must be made to the highly carburised steel used for the manufacture of dies. Such steel should contain 0.8 to 1 per cent. of carbon and no manganese. It is usual to water-harden and temper it to a straw colour, and a really good die will strike 40,000 coins of average dimensions without being fractured or deformed, but if the steel contain 0.1 per cent. too much carbon, it would not strike 100 pieces without cracking, and if it contained 0.2 per cent. too little carbon, it would probably be hopelessly distorted and its engraved surface destroyed in the attempt to strike a single coin.

The above examples will be sufficient to show how diverse are the properties which carbon confers on iron, but, as Faraday said in 1822, "it is not improbable that there may be other bodies besides charcoal capable of giving to iron the properties of steel." The strange thing is that it is not known with any certainty whether, in the absence of carbon, other elements do play the part of that metalloid in enabling iron to be hardened by rapid cooling. Take the case of chromium, for instance; chromium-carbon steels can, as is well known, be energetically hardened, but

Busek* has asserted that the addition of chromium to iron in the absence of carbon does not enable the iron to be hardened by rapid cooling. Probably by employing the electrical method of heating adopted by Pepys a decision will be arrived at as to the hardening properties of elements other than carbon.

A few words must be devoted to the consideration of the colours which direct the artist in tempering or reducing the hardness of steel to any determinate standard. The technical treatises usually give, not always accurately, as Reiser† has shown, a scale of temperature ranging from 220° to 330°, at which various tints appear passing from very pale-yellow to brown-yellow, purples, and blues to blue tinged with green, and finally to grey. Barus and Strouhal point out‡ that it is possible that the colour of the oxide film may afford an indication of the temper of steel of far greater critical sensitiveness than has hitherto been supposed. It is, however, at present uncertain how far time, temperature, and colour are correlated.

That the colours produced are really due to oxidation was shown by Sir Humphry Davy in 1813,§ but the nature of the film has been the subject of much controversy. Barus points out that "the oxygen molecule does not penetrate deeper than a few thousand times its own dimensions," and that it probably passes through the film by a process allied to liquid diffusion. The permeable depth increases rapidly with the temperature until, at an incipient red heat, the film is sufficiently thick to be brittle and liable to rupture, whereupon the present phenomenon ceases or is repeated in irregular succession.

Summary.—Looking back over all the facts dealt with in this chapter, it will be evident that two sets of considerations are of special importance—(1) those which belong to the relations of carbon and iron, and (2) those which contemplate molecular change in the iron itself. The first of these has been deliberately subordinated to the second, although it would have been possible to have written much in support of the view that carburised iron is an alloy of carbon and iron, and to have traced with Guthrie the analogies which alloys, in cooling, present to cooling masses of igneous rocks. This view has been developed with much

* *Stahl und Eisen*, vol. ix. (1889), p. 728.

† *Das Härten des Stahles*, p. 78 (Leipzig, 1881). See also Löwenherz, *Zeitschrift für Instrumentenkunde*, vol. ix. (1889), p. 322.

‡ *Bull. U.S. Geo. Survey*, No. 27 (1886), p. 51.

§ Sir Humphry Davy, *Thomson's Ann. Phil.*, vol. i. (1813), p. 131, quoted by Turner, *Proc. Phil. Soc. Birmingham*, vol. vi. (1889), part 2.

ability by Howe,* who even suggests mineralogical names such as "cementite," "pearlyte," and "ferrite" for the various associations of carbon and iron.

Such analogies present considerable interest, but the possibility of molecular change in the iron itself, which results in its passage into a distinctive form of iron, is at present the more important subject for consideration, not merely in relation to iron, but as regards the wider question of allotropy in metals generally.

Many facts noted in spectroscopic work will, as Lockyer has shown, have indicated the high probability that the molecular structure of a metal like iron is gradually simplified as higher temperatures are employed. These various simplifications may be regarded as allotropic modifications.

The question of molecular change in solid metals demands continued and rigorous investigation. It is well known what important discoveries have been made in chemistry by the recognition of the fact that the elements act on each other in accordance with the great law of Mendeléef, which states that the properties of the elements are periodic functions of their atomic weights. There is little doubt but that it will be shown that the relation between small quantities of elements and the masses in which they are hidden, is not at variance with the same law. It has elsewhere been shown that this may be true, by a study of the effect of small quantities of impurity on the tenacity of gold, and the probability that it may prove true in the case of iron has also been dealt with in the previous chapter.

The future of steel will depend on the care with which the nature of the influence exerted by various elements on iron is investigated, and by ascertaining the thermal treatment to which it may most suitably be subjected.

Is it not strange that so many researches should have been devoted to the relations between carbon, hydrogen, and oxygen in organic compounds, so few to the relations of iron and carbon, and hardly any to iron in association with other elements? The reason for the comparative neglect of metals as subjects of research arises from the belief that methods which involve working at high temperatures are necessarily inaccurate, but the school of Ste. Claire-Deville has shown that they are not, and there are signs that our traditional love for the study of metals is reviving.

* *Engineering and Mining Journal*, vol. xlv. (1888), p. 131. See also *The Metallurgy of Steel*, vol. I. (New York, 1890), p. 165.

CHAPTER V.

FUEL AND THERMAL MEASUREMENTS.

Classification of Fuel.—The term fuel is applied to substances that may be burned by means of atmospheric air with sufficient rapidity to evolve heat capable of being applied to economic purposes. Only those substances that contain a large proportion of carbon and hydrogen can be used economically. In some cases the products of combustion are used for effecting metallurgical reactions; in most cases, however, the fuel is consumed simply for the sake of the heat generated.

Fuels may be of ancient or modern origin, and may be divided into two classes—(I.) Natural fuels and (II.) Prepared fuels.

The first class includes—(1) wood and the various kinds of mineral fuel, (2) turf or peat, (3) lignite, (4) bituminous coal, and (5) anthracite. Besides these, various liquid hydrocarbons, such as petroleum, are found in sufficient quantity to render their employment possible on a large scale. At Pittsburgh in Pennsylvania, and at other localities in the United States, combustible gas occurs naturally, and is largely used for metallurgical purposes.

The second class includes—(1) compressed fuels, which are composed of more or less pulverulent material consolidated into bricks, with or without cementing agents; (2) dried fuels, or those in which the water and a certain proportion of the more volatile constituents have been expelled by heat, examples being afforded by wood, lignite, and peat; (3) carbonised fuels, such as coke and charcoal; and, lastly, (4) liquid and gaseous fuels, obtained (a) by the distillation, partial or entire, of natural fuels, or (b) by their incomplete combustion.

The value of all these fuels depends upon the amount of carbon and hydrogen they contain. The majority of them contain oxygen, nitrogen, sulphur, and phosphorus, as well as a certain amount of inorganic material which ultimately forms the ash. The amount and nature of this ash is of great importance, and it will be evident that, if the fuel can be deprived of its ash-giving

constituents by treatment before combustion, its value will be greatly increased. The hydrogen that is in excess of the quantity required to form water with the oxygen in the fuel is alone available for combustion, and is termed the *disposable* hydrogen. The remainder of the hydrogen is regarded as being already in combination as water, and may be viewed as an actual source of loss, because this water has to be vaporised when the fuel is burned. Cellulose ($C_6H_{10}O_5$) contains no disposable hydrogen, whilst cannel coal contains a considerable quantity.

The temperature at which fuels kindle varies considerably, since an initial temperature is required before combustion is effected. Slow oxidation may, it is true, take place at ordinary temperatures, but in metallurgical practice it is only comparatively rapid combustion that is really useful. Extreme density and, on the other hand, great tenuity equally hinder inflammability. For the former reason, anthracite, diamond, and graphite are ignited with great difficulty. Fuels richest in hydrogen are the easiest to light, the inflammability of resinous wood and of bituminous coal being due to this fact. Combustible gases, however, do not ignite below a cherry-red heat, on account of the extreme dispersion of their molecules.* The inflammability of vegetable charcoal depends upon the temperature at which it is prepared. Thus, when wood is carbonised at 300° to 400° , the charcoal ignites at 360° ; and when a temperature of 1200° to 1300° has been employed, ignition cannot be effected below 600° to 800° . This is due to the fact that the hydrogen is driven off almost entirely at the higher temperatures. Peat ignites at 225° ; pine wood at 295° ; ordinary coal at 325° , the melting-point of lead; coke, anthracite, hydrogen, and carbonic oxide at a dull-red heat.

The length of flame given by fuel in burning is so important that coals have advantageously been classed as "long-flaming" and "short-flaming." Certain fuels disengage at the moment of combustion a large proportion of volatile matter, and these constitute the long-flaming varieties. The manner in which the fuel is burned, however, has a great effect upon the flame. Charcoal, for example, if burned with free access of air, merely glows; but if burnt with a limited supply of air in a thick layer so arranged that the products of combustion from the lower portion pass through the upper, carbonic oxide will be formed, which will burn with a blue flame. The volume of the flame depends, amongst other conditions, upon the velocity of the current of air

* Frankland, *Phil. Mag.*, vol. xxxvi. (1868), p. 309. See also Ernst, *Chemisches Repertorium*, vol. xvii. p. 2.

by which the combustion is effected, the volume decreasing as the velocity rises.

Calorific Power.—The calorific power of a fuel is the total heat generated by the combustion of a unit of weight of the fuel. The heat is measured in two ways, either by the number of units of weight of water raised 1° , or by the number of units of water evaporated. The latter method, which was proposed by Professor Rankine, gives numerical results 537 times less than the former. In expressing the calorific power of a fuel, the amount of heat generated on the combustion of carbon to carbonic anhydride is taken, as the standard of comparison. This calorific power of carbon is expressed by the number of parts by weight of water capable of being heated from 0° to 1° by the combustion of one part by weight of carbon. It is found by direct experiment to be 8080 units. The unit of heat varies with the thermometric scale and the unit of weight employed. The unit most largely adopted, the metric unit or *calorie*, is the quantity of heat required to raise 1 kilogram of water from 0° to 1° C.; whilst the British thermal unit is the amount of heat required to raise 1 lb. of water one degree Fahr. Thus 1 *calorie* = 3.96832 British units, and 1 British unit = 0.251996 *calorie*. Expressed in equivalent foot-pounds, 1 *calorie* = 1390.

For experimentally determining the calorific power of a fuel, a calorimeter is employed. Count Rumford's calorimeter consisted simply of a vessel, filled with water, containing a worm-pipe, through which the products of combustion passed from a funnel outside. In this way they imparted their heat to the water, whose rise in temperature was noted. All calorimeters are similar in principle to Rumford's. In the more modern instruments, however, the vessel in which the combustion takes place is entirely surrounded by water and by an air jacket.*

If a fuel consists only of carbon and hydrogen, its calorific power may be calculated by multiplying the weight of each of the elements in one part of the fuel by their respective calorific powers as found by experiment. For example, a fuel consists of 85.71 per cent. of carbon and 14.29 per cent. of hydrogen. What is its calorific power? The calorific powers of carbon and hydrogen are respectively 8080 and 34,462, and

$$85.71 \times 8080 = 692536.80$$

$$14.29 \times 34462 = 492461.98$$

$$\hline 1184998.78$$

* On calorimeters, consult Ganot's *Physics*; Watts' *Dictionary of Chemistry*; *Zeit. anal. Chem.*, vol. xxiii. p. 453; *Journ. Soc. Chem. Ind.*, 1886, p. 635; F. J. Rowan, *ibid.*, 1888, p. 195.

which is the heat evolved on the combustion of 100 parts of the fuel. This, when divided by 100, gives 11,849.98 as the calorific power of the fuel. So simple a case as this is rarely met with, it being usually necessary to determine the amount of disposable hydrogen in the fuel, and to multiply the result by 34,462.

Scheurer-Kestner* has shown that carbon in combination develops more heat than carbon in the form of charcoal. Consequently the calculated values of the calorific powers of coals are, as a rule, too low. In order to obtain results approximating more closely to the truth, it is advisable to employ for carbon the calorific power of 9000 instead of 8080, and for hydrogen the number 30,000 instead of 34,642. Even this correction does not apply to certain bituminous lignites, and actual experiment is the only safe guide for commercial purposes.

Calorific Intensity.—The calorific intensity, or pyrometric effect of a fuel is the highest temperature which the fuel is capable of producing when burnt in air. Measurements of calorific intensity are based on the fact that the heat produced by combustion is transferred to the product of combustion, and it may be determined by calculation on the assumption that the calorific intensity of a simple combustible body burnt in oxygen is equal to its calorific power divided by the product of the relative weight of its products of combustion and the specific heat of those products, or, expressed as an equation,

$$t^{\circ} = \frac{W \times C}{w \times c}$$

where W represents the weight of the substance, C the calorific power of the substance, w the weight of the product of combustion, and c its specific heat. For example, the calorific intensity of carbon burnt to carbonic anhydride in oxygen, is—

$$\frac{12 \times 8080}{(12 + 32) \times 0.22} = 10015^{\circ}.$$

The calorific intensity of carbonic oxide burnt to carbonic anhydride is—

$$\frac{28 \times 2403}{(28 + 16) \times 0.22} = 6950^{\circ}.$$

If the substance is a mixture, the weights and specific heats of

* *Revue scientifique*, 1888; translation in *Journ. Soc. Chem. Ind.*, 1888, p. 615; *Bull. de la Soc. industrielle de Mulhouse*, 1875, p. 241; *Comptes Rendus*, vol. lxvi. (1868), pp. 1047, 1220; vol. lxvii. (1868), pp. 659, 1002; vol. lxviii. (1869), p. 608; vol. lxix., p. 412.

the various products of combustion must be introduced. In determining the calorific power of hydrogen, the water obtained is assumed to be in the liquid state. In determinations of the calorific intensity, however, the water is in the form of gas. From the calorific power, therefore, must be subtracted the amount of heat which would be given out on cooling the steam to 0° . For one part of water at 100° this would be 537 *calories*. Again, in raising the product of combustion from 0° to t° , a greater amount of heat will be needed to raise it the first 100° while that product is liquid than would have been required if it had been gaseous. These two amounts of heat are in the proportion of the specific heats of steam and water, that is, as 0.4805 is to 1. Hence the extra quantity of heat to be added to the 537 *calories* is $(1 - 0.4805) 100$, or 51.95 *calories*. The calorific power must, therefore, be decreased by $(51.95 + 537) 9$, or 5300.5 *calories*, since 1 part of hydrogen yields 9 parts of water. Hence the calorific intensity of hydrogen is—

$$\frac{1 \times (34462 - 5300.5)}{9 \times 0.4805} = 6743^{\circ}.$$

The calorific intensity is merely a theoretical quantity, as it is based on the assumptions that the products of combustion of the fuel have constant specific heats for all temperatures, and that they absorb all the heat produced. Neither of these assumptions is true, inasmuch as the specific heats of gases generally increase with the temperature, and as there is also a considerable amount of heat lost by conduction and by radiation, and dissociation limits the temperature. The computation of calorific intensity has consequently but little commercial value.

The calorific intensity of a fuel may be found by direct experiment by means of *pyrometers*. These are thermometers so constructed as to measure high temperatures.

Pyrometry.—This term is applied to the measurement of high temperatures. It is not possible, it is true, to attain as accurate measurements of high temperatures as it is of low ones by the aid of thermometers; nevertheless, very precise determinations have been made, and, as the measurement of high temperatures is of great importance in metallurgy, some attention must be devoted to the principles on which pyrometry is based.

The author has elsewhere pointed out* that, notwithstanding the importance attached by early experimenters to the action of

* Lecture at the Royal Institution. *Nature*, vol. xlv. 1892 p. 534.

heat on metals, they had but little definite information respecting the relative degrees of intensity of heat; and their views were not inadequately expressed in the eighth century by Geber, who stated that great difficulties arose in conducting operations with the aid of heat, because heat cannot be measured, "*sed quoniam non est res ignis, quæ mensuari possit.*"* The name of Josiah Wedgwood is always associated with the early attempts to provide a practical method of pyrometry; but, although he wrote a thousand years after Geber, he seems to have merely changed the language of the latter, "heat cannot be measured," into a lament that there were no trustworthy instruments for effecting the measurement of "the higher degrees of heat, from a red heat up to the strongest that vessels made of clay can support."† He therefore devised a pyrometer, which depended on the contraction that clay experiences when strongly heated. It is not necessary to give a history of pyrometry in this place; the author would merely point out that Wedgwood demonstrated the necessity for the accurate measurement of high temperatures, and that, from his time, the invention of more or less suitable instruments has proceeded rapidly.

In the long interval between the work of Wedgwood and that of the late Sir William Siemens, such pyrometric appliances as were actually in industrial use depended mainly on what is known as the "method of mixtures,"—that is, upon the employment of a body, the specific heat of which was known, to transfer or carry heat from a furnace, or source of heat, to a measured volume of water, the rise in temperature of which was indicated by an ordinary thermometer. Pyrometers depending on the expansion of metallic strips or rods are also employed; but they may all be set aside with the general statement that, although they are useful in affording rough approximate measurements, they are useless for accurate pyrometry. It may be well to add that a noteworthy advance in thermometry has recently been made in Professor Ramsay's laboratory at University College, by Messrs. Baly and Chorley, who employ the fluid alloy of sodium and potassium, instead of the mercury of the ordinary thermometer; and, as temperatures of 600° Centigrade may thus be measured by making the thermometers of very hard glass, further details of their experiments will be looked for with much interest.

Weinhold‡ has thus briefly set forth the principles on which pyrometers have been constructed:—

* From the edition of his *Summa Perfectionis Magisterii*, published in Venice, 1542, p. 28. (Additions have probably been made to Geber's original text.)

† *Phil. Trans. Royal Soc.*, vol. lxxii. 1782, p. 305.

‡ *Pogg. Ann.* vol. cxlix. (1873), p. 186.

- | | |
|---|---|
| <ol style="list-style-type: none"> 1. Change in the volume of bodies— <ol style="list-style-type: none"> (a) Contraction of a solid body; (b) Expansion of solid bodies, or of gases. 2 Change in the physical state of bodies. 3 Conduction of heat by solid bodies. | <ol style="list-style-type: none"> 4. Radiation of heat. 5. Production of thermo-electric currents. 6. Change in the electrical resistance of conductors. 7. Calorimeter methods. 8. Dissociation of chemical compounds. |
|---|---|

Carl Barus * has given the following more extended classification in an admirable treatise on the measurement of high temperatures :—

- | | |
|---|--|
| <ol style="list-style-type: none"> 1. Dilatation of solids— <ol style="list-style-type: none"> (a) A single solid; (b) Two solids acting differentially. 2. Dilatation of liquids. 3. Dilatation of gases— <ol style="list-style-type: none"> (a) Expansion measured in volume, manometrically; (b) Expansion measured in pressures, manometrically; (c) Expansion measured in volume, by displacement. 4. Vapour tension. 5. Dissociation. | <ol style="list-style-type: none"> 6. Fusion. 7. Ebullition. 8. Specific heat. 9. Heat conduction. 10. Heat radiation. 11. Viscosity— <ol style="list-style-type: none"> (a) of solids; (b) of liquids; (c) of gases. 12. Spectrophotometry and colour. Rotary polarisation. 13. Acoustics (wave length). 14. Thermo-electrics. 15. Electrical resistance. 16. Magnetic moment. 17. Miscellaneous. |
|---|--|

This classification shows that almost every thermal phenomenon has been utilised for pyrometry. It is especially necessary for the student to know what appliances afford a means of estimating high temperatures with sufficient accuracy for the ordinary purposes of a metallurgical works, and are at the same time sufficiently durable to withstand rough usage. For delicate investigations there are several instruments that can safely be adopted. These will be described subsequently.

The simplest methods are undoubtedly grouped in class 6 of Barus "fusion." For instance, the insertion of a fragment of metal of known melting-point in the locality whose temperature is to be tested will often afford at once the required information. Thus, the temperature of the hot blast may be capable of melting a rod of lead (melting-point 335°), though it may fail to melt a similar rod of zinc (melting-point 412°). A strip of pure silver will just

* *Bulletin of the United States Geological Survey*, No. 54, Washington, 1889. This contains an exhaustive bibliography of pyrometry.

melt at a temperature at which zinc boils, and this has been accurately determined as being 954° , and it follows, therefore, that a temperature which will just melt pure silver may safely be taken to be about 950° .

Many appliances, notably such as that devised by Weinhold,* may be purchased, the action of which depends upon the method of mixtures (No. 8 in Barus' scheme). In such appliances a "carrier" of platinum, iron, or clay transfers heat from the furnace to a known weight of water, the increase in temperature of which affords a means of calculating the unknown temperature. The method of mixtures has even been applied to gases. The hot blast supplied to a furnace is cooled with a known amount of cold air, of which the increase in temperature may easily be ascertained by means of an ordinary thermometer, and the temperature of the hot blast calculated.

For rapid determinations of high temperatures in works the pyrometer of Carnelly and Burton† (class 9 of Barus) may advantageously be used. It is cheap, and does not readily get out of order; moreover, when once placed in position, it requires little or no manipulation except the reading off of a couple of thermometers and a reference to a table. The principle on which it is based is as follows:—If a current of water of known temperature be allowed to flow at a constant rate through a coiled metallic tube, placed in the space the temperature of which is required, then the increase in the temperature of the outflowing water will be greater the higher the temperature of the space.

Fig. 44 illustrates the form of the new pyrometer and the method of using it. A is a coil of copper tubing placed in the space, M, of which the temperature is required. A current of water flows from the cistern C, through the coil A, into the glass tube B, and out at the nozzle *f*. The tube F attached to the water-main, feeds the receptacle at such a rate as to maintain a small but continual overflow through the tube G, which is connected with the waste-pipe. In this way a uniform head of water is obtained, so that the current flows through the coil at a constant rate. The effluent branch of the copper coil projects such a distance into the tube B, that the issuing water flows directly on to the bulb of the thermometer D. The two thermometers, E and D, serve to determine the temperatures of the inflowing and outflowing water. They are graduated to $\frac{1}{2}^{\circ}$, so that temperatures can easily be read off to $\frac{1}{10}^{\circ}$. The copper tube has an

* *Pogg. Ann.*, vol. cxlix. (1873), p. 209.

† *Journ. Chem. Soc.*, vol. xiv. (1884), p. 237.

internal diameter of 6 millimetres. The coil, which has five complete turns, is 8 centimetres high, and has an external diameter of 8 centimetres. The head of water in the receptacle C, above the outflow *f*, was 20 centimetres in the inventors' experiments, the average flow of water at a temperature of 80° being 813 cubic centimetres per minute measured at a temperature of 10°.

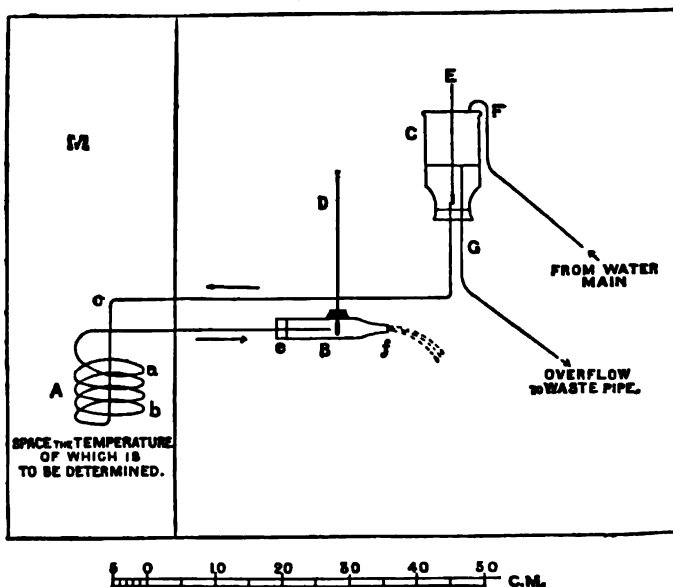


FIG. 44.

From a number of experiments made for the purpose of graduation, Carnelly and Burton deduced a mean curve showing the relation between the temperature of the furnace and the increase in temperature of the effluent water. When once the pyrometer is placed in position in any given furnace, a certain increase in the temperature of the effluent water will always indicate to the operator that a desired temperature has been reached, independently of any knowledge of what that particular temperature may be as measured on an ordinary thermometric scale. Each instrument and every variation in the head of water will of course require a distinct table; but when once the

instrument is fixed, and supplied with a constant head of water, one table will be all that is necessary. As, however, in most metallurgical operations the actual temperature in so many degrees is not necessarily required, it will be sufficient for the workmen to know the increment in temperature of the out-flowing water, and he would soon accustom himself to represent all the different states of the furnace in terms of this increment.

A new era in the measurement of heat began with the work of Sir William Siemens. He showed* that electrical resistance might be used practically in pyrometry. Fig. 44*a* gives a general view of

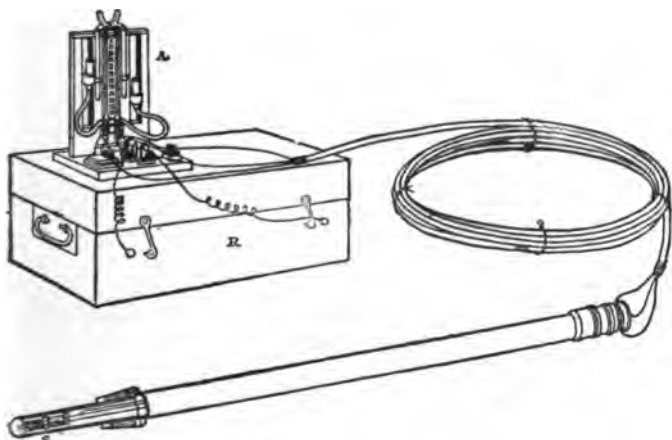
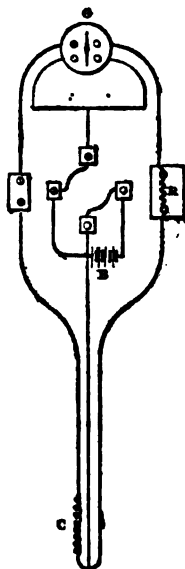


FIG. 44*a*.

his apparatus, and its nature is explained by the accompanying diagram, Fig. 44*b*. A divided current passes from the battery B to a platinum wire C (coiled round a clay cylinder), and to a resistance-coil R. At the ordinary temperature, the resistance of the platinum coil is balanced by the standard resistance R, and an equal current will flow through each. If, however, the platinum coil C be heated, its resistance will be increased, and this increase of resistance can be measured in various ways. Siemens adopted for use in works a small voltmeter, shown at A, Fig. 44*a*; the current sent through the platinum coil *c* was of sufficient strength to decompose acidulated water, and the difference in the amount of water decomposed by that portion of the current which passed through the heated coil, as compared with that decomposed

* Collected papers.

by the current transmitted through the standard resistance at R, Fig. 44*b*, gave, on reference to a table, the temperature to be determined. For many years this electrical-resistance pyrometer was the only appliance, believed to be trustworthy, which could be placed in the hands of artificers. Its usefulness was widely recognised, and a Committee of the British Association was appointed to report upon it. The result of the inquiry*

FIG. 44*b*.

rather tended to shake confidence in the instrument, as it was shown that it was liable to changes of zero. Mr. H. L. Callendar† has, however, done much to prove that, with certain precautions, the method may be rendered very trustworthy. He winds the platinum wire on a plate of mica, excludes reducing gases, as the Committee suggested, by enclosing the coil in a tube of doubly-glazed porcelain, and uses a zero method for measuring the resistances with the galvanometer.

* *British Association Report*, 1874, p. 242.

† *Phil. Trans. Royal Soc.*, vol. clxxviii, 1887, p. 161.

Fig. 44c represents, somewhat diagrammatically, the arrangement of the apparatus.*

A B, B C are equal resistances, forming the arms of the balance. The battery is connected at A and C, and one terminal of the galvanometer G at B. DE represents a set of resistance coils, which, together with the resistances AB and B C, may be supplied by an ordinary box of coils of the "post-office" pattern. F K represents a straight bridge-wire, with a divided scale attached. The other terminal of the galvanometer is connected to the contact-piece H, which slides along this wire. The leads A M, K N, from the pyrometer coil P, are connected to A and K; and the compensating leads O L, L D, the resistance of which is equal to A M, K N, are connected to C and D. These four leads may be of any convenient length; they are symmetrically arranged, so that corresponding parts are always at the same temperature. When the balance is found by inserting suitable resistances in the arm DE, and sliding the contact-piece H, it is plain that, since the

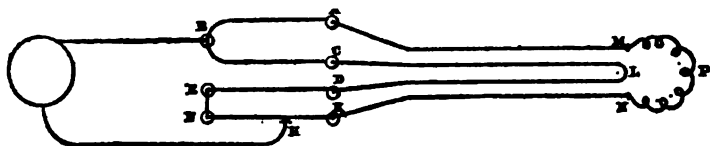


FIG. 44c.

resistances A B, B C, are equal, the resistance of the pyrometer and its leads, together with that of the length H K of the bridge-wire, will be equal to the remaining portion F H of the bridge-wire, together with the coils D E, and the compensation C L D. Thus, the changes of the resistance of the pyrometer-leads A M, K N, are compensated by the equal changes in the leads C L, L D, and the resistance of the pyrometer-coil itself is directly given by the sum of the coils D E, and the reading of the bridge-wire. The resistance of a centimetre of the bridge-wire F K is made to correspond to such an increase of the resistance of the pyrometer coil P, as is produced by a rise of 1° C. The contact key H slides along this wire, and the galvanometer can easily be made sensitive to one-hundredth of a centimetre of this bridge-wire; so that one-tenth of a centimetre, which corresponds to one-tenth of a degree, can, of course, be measured with certainty. The author has worked for several days at the Royal Mint with Mr. Callendar, and is satisfied that, at temperatures exceeding that

* *Phil. Magazine*, vol. xxxii. 1891, p. 104, and vol. xxxiii. 1892, p. 220.

of bright redness, the comparative readings are accurate to one-tenth of a degree. This would have been considered impossible a few years ago, and the statement will, perhaps, be received with some incredulity. Later on, evidence will be examined which leads to the belief that, in the measurement of a "white-heat," degrees of value similar to those of the ordinary mercurial thermometer are still employed.

Measuring the increased resistance of a heated conductor is not the only way in which electricity has been made serviceable in the measurement of high temperatures. It has long been known that if a junction of two metals be heated, the electrical equilibrium of the system is disturbed, and the measurement of the difference of potential produced affords a means of estimating the temperature of the junction. The use of such thermo-junctions appears to have been suggested by A. C. Becquerel in 1826, and adopted by Pouillet* ten years later. Unfortunately, the metals composing the thermo-junctions were badly chosen, and their use was consequently greatly retarded until, within the last few years, Professor H. Le Chatelier,† of the École des Mines, Paris, advocated the use of platinum, in conjunction with platinum alloyed with 10 per cent. of rhodium. The author first adopted this couple in 1889, and has since constantly used it, in conjunction with a photographic recorder, devised for the purposes of an investigation which was entrusted to him by the Institution of Mechanical Engineers. C. Barus has shown that the indications afforded by thermo-junctions are trustworthy at very high temperatures, and he has enabled great confidence to be placed in the platinum-platinum-iridium thermo-junction originally suggested by Tait. In its latest form, the instrument consists of two wires, one of the metal, and the other of the alloy mentioned above, simply twisted at their ends or soldered with gold, and connected with a dead-beat galvanometer of about 200 ohms resistance. The suspended coil galvanometer, particularly the later types of this instrument, is admirably adapted for use with this thermo-couple.

The Fig. 38 shows the couple arranged for determining the temperature of a cooling mass of steel in a research to which reference has been made in Chapter IV. of this volume.

The deflections of the galvanometer may be converted into thermometric degrees by Tait's empirical formula—

* *Comptes Rendus*, vol. iii. (1836), p. 782.

† *Bull. Soc. Chim. Paris*, vol. xlvii. (1887), p. 2; *Journ. de Physique*, vol. vi. (1887), p. 23.

$$E = A (T_1 - T_0) + B (T_1^2 - T_0^2),$$

in which E is the electro-motive force in terms of the absolute temperature T_1 and T_0 of the two elements of the couple. It is only necessary to introduce into this formula the values of E corresponding to two fixed points, in order to determine the co-efficients A and B , and to construct a table of ordinary temperatures corresponding to each millimetre of the scale. Le Chatelier, however, showed that the second term of the equation (a parabola) ceased to be of importance with the platinum, platinum-rhodium couple for high temperatures, and that between

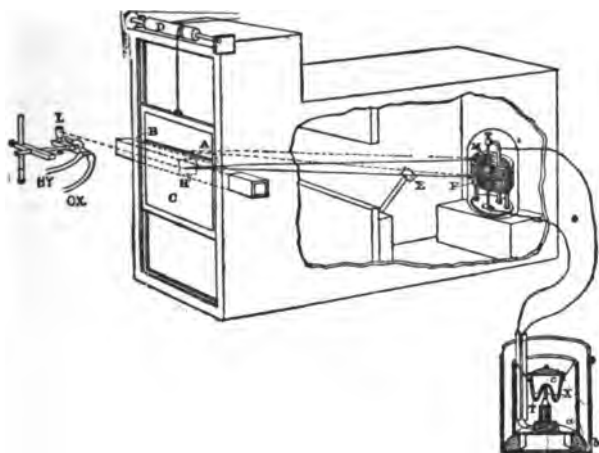


FIG. 44d.

300° and 1200° the equation becomes approximately that of a straight line:

$$E = a + bt,$$

in which E is the electro-motive force, t the observed temperature, and a and b numerical co-efficients.*

The arrangement, which is shown in Fig. 44d, consists of a galvanometer of the above-mentioned type enclosed in a large camera; a fixed mirror F is placed below the movable mirror M of the galvanometer, so that the light from the lime cylinder L , reflected in the mirror H , passes to both mirrors, F and M , and is reflected in the direction of a fine horizontal slit $A B$, behind which a sensitised photographic plate C is drawn vertically past

* For a further development of this formula, see Osmond, *Transformations du Fer et du Carbone* (Paris, 1888), p. 16.

the slit, by means of gearing D driven by clockwork. The ray from the fixed mirror is interrupted periodically by the vane E, and a beaded datum-line is given, which enables any irregularity in the advance of the plate to be detected.

The amount of divergence, from its datum-line, of the spot of light reflected by the movable mirror at any given moment, bears a relation (which can readily be found by calibration) to the temperature to which the thermo-junction X is heated; and the variations of temperature are denoted by a curve which is the resultant of the upward movement of the plate and the horizontal movement of the spot of light. A crucible c which may be filled with molten metal, is provided with a tubulure T for the insertion of the thermo-junction. The crucible is suspended by wires in a double jacket of tin plate, a, b.

It will be obvious that the moving plate C may be replaced by a revolving cylinder driven by internal clockwork. This cylinder may be covered with sensitised paper, and a continuous record of the temperature of any furnace may be obtained provided a thermo-junction is placed in the furnace. Such an arrangement has already been described by the author* as applicable to the measurement of the temperature of hot-blast stoves, and experiments are now being carried out at the New Dowlais Works, Cardiff, with the aid of such an appliance. The appliance has, in fact, been found to be most useful, and full details respecting it will be found in the papers referred to.†

The author is satisfied that this thermo-junction readily affords trustworthy results, accurate to 1° , at temperature^s of over 1000° , and it may be made accurate to $\frac{1}{10}^{\circ}$. One important feature is the small space occupied by the thermo-junction, which may be suitably protected, and inserted into the midst of a very small mass of metal. The pyrometer is calibrated by exposing the thermo-junction to certain known temperatures, such as the solidifying points of salts or metals. There is no difficulty in recognising the melting or the solidifying points; for, as the mass passes from the solid to the fluid state, the temperature remains constant for a brief period, the duration of which depends on the amount of material operated upon, and its latent heat of fusion; the result being that the spot of light from the galvanometer will be arrested and the position on the scale, at which it stops, marks the temperature to be determined.

The electromotive-force produced by heating the thermo-junction

* *Journal Iron and Steel Inst.*, Part. II. 1892, p. 33.

† *Ibid.*, Part I. 1893. p. 112.

to any given temperature, is measured by the movement of the spot of light on the scale, and, as has been above indicated, the scale is calibrated by heating the thermo-junction in contact with substances of known melting points.

The following list gives a sufficient number of such fixed points, which have been established by concurrent evidence of various kinds:

100° Centigrade	.	.	Boiling point of water.
326°	"	.	Melting point of lead.
358°	"	.	Boiling point of mercury.
415°	"	.	Melting point of zinc.
448°	"	.	Boiling point of sulphur.
625°	"	.	Melting point of aluminium.
665°	"	.	Boiling point of selenium.
954°	"	.	Melting point of silver.
1015°	"	.	" " potassium sulphate
1045°	"	.	" " gold.
1054°	"	.	" " copper.
1500°	"	.	" " palladium.
1775°	"	.	" " platinum.

They rest mainly, however, on determinations made with the air-thermometer.

Some years ago, Carnelly* determined the melting-points of certain substances by the method of mixtures, and used them, when enclosed in capillary tubes of glass, to ascertain at what temperatures substances of unknown melting-points actually fuse. Le Chatelier† has since tested with the aid of his thermo-couple, the accuracy of Carnelly's experiments, and has obtained in many cases very concordant results, as is shown in the following table:—

* *Journ. Chem. Soc.*, vol. xxxiii. (1878), pp. 273, 281; vol. xlv. (1884), p. 237.

† *Bull. Soc. Chim. Paris*, vol. xlvii. (1887), p. 300.

Pouillet's Scale

Incipient red	525° C	= 977° F
Dark red	700 "	= 1292 "
Incipient Cherry red	800 "	= 1472 "
Clear cherry red	1000 "	= 1832 "
White	1300 "	= 2372 "
Gleaming white	1500 "	= 2732 "

TABLE OF MELTING-POINTS.

	Le Chatelier.	Carnelly.
Potassium chloride	740°	734°
Sodium "	775	772
Calcium "	755	719
Barium "	847	772
Tin (SnCl_2) "	840	812
Sodium carbonate	810	814
Barium "	795	
Potassium "	885	834
Sodium sulphate	867	861
Barium nitrate	592	
Potassium sulphate	1015	
Potassium bichromate	975	
Sodium phosphate	957	
Potassium chlorate	370	359
Cuprous sulphide	1100	
Pure white pig-iron	1135	
Grey pig-iron	1240	
Grey forge pig-iron	1220	
Nickel	1420	

The melting-points of silver, 945° , of gold, 1045° , and of palladium, 1500° , may be conveniently remembered in connection with the above table.

The student is thus placed in possession of a number of melting-points which may safely be trusted.

For really accurate measurements in scientific research, the modification of the air thermometer devised by Deville and Troost may safely be adopted.* With regard to it, modifications of the air thermometer in which glass bulbs were replaced by metal were adopted by Prinsep and others early in the present century. The great advance Deville and Troost made was the substitution of bulbs of porcelain for those of metal. The following is an outline of their experimental method:—

Their apparatus consists of a globular flask of Bayeux porcelain of 280 or 300 cubic centimetres capacity, with a neck 11 centimetres long and 4 millimetres in internal diameter. A quantity of iodine is put into the flask, and the neck is nearly closed by a small plug of porcelain, which lies loosely in the opening. When the flask is now exposed to a high temperature, the

* Descriptions of pyrometers for measuring hot-blast temperatures will be found in *Journ. Iron and Steel Inst.*, 1884, pp. 195, 240; 1885, p. 325; 1886, p. 207; 1888, No. 2, p. 110; *Proc. Inst. M.E.*, 1852, p. 53; *Journ. Soc. Chem. Ind.*, 1885, p. 40.

Iodine is vaporised, and the greater part escapes by the neck, driving out at the same time nearly the whole of the air. After the flask has been exposed for about twenty minutes to the temperature that is to be measured, the flame of an oxy-hydrogen blowpipe is allowed to play for an instant on the porcelain plug lying in the neck; the plug is thus melted, and closes the flask hermetically. When cold the flask is cleaned and carefully weighed; the end of the neck is broken under boiled water or mercury, and the flask is weighed, together with the water or mercury which enters; it is then completely filled with water or mercury and weighed again; lastly, the flask is weighed when empty. From the weights thus obtained it is easy to calculate the capacity of the flask and the volume of the residual air, that is, air which has not been expelled by the iodine vapour. The first weighing gives directly the excess of weight of the flask and iodine vapour over that of the empty flask. The observations which require to be made in each experiment are the following:—

Temperature of the balance . . .	t°
Pressure of the atmosphere . . .	h millimetres
Excess of weight of sealed flask and iodine vapour at end of ex- periment over that of the empty flask	i grms.
Capacity of flask	v cubic centimetres
Residual air	a " "

In order to be able to calculate the exact temperature at which the flask was sealed the following constants are necessary:—

Weight of 1 c.c. air at 0° and 760 mm. pressure	= 0.001293 grm.
Density of iodine vapour referred to air as unity	= 8.716 grms.
Co-efficient of expansion of air for 1° C. . . .	= 0.00366 grm.
Co-efficient of cubical expansion of the porcelain for 1° C.	= 0.0000108 "

The required temperature may then be calculated in the following manner:—

Let $I_w = \left(\frac{(v-a)0.001293}{(1+0.00366 t)} \frac{h}{760} + i \right)$ be the total weight of iodine vapour contained in the flask at the moment of sealing; then

$$\frac{I_w}{0.001293 \times 8.716} \frac{(1+0.00366 T) 760}{h} = I_v$$

will be the volume of the vapour at the same moment; but

$$I_v + \frac{a(1+0.00366 T) 760}{(1+0.00366 t) h} = v(1+0.0000108 T),$$

and from this equation, in which T , the temperature required, is the only unknown quantity, its value is easily found.

Owing to the belief that the molecule of iodine undergoes dissociation at high temperatures, this method has been modified, atmospheric air being used in place of iodine.

Barus has devised a form of appliance which he considers to be superior to that used by Deville for determining the boiling-points of metals. As shown in Fig. 45, it consists of a glazed tube of

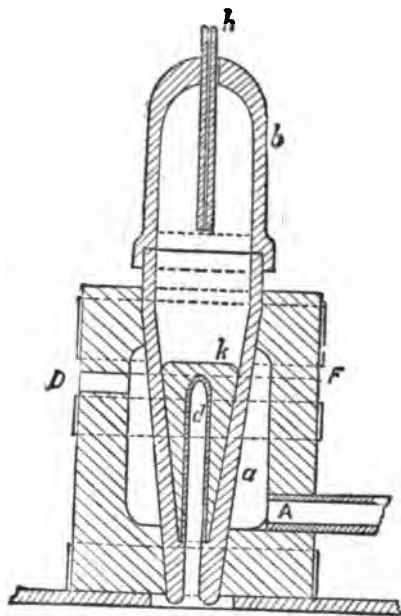


FIG. 45.

porcelain, *d*, passed through a hole in the base of a crucible, *a*. The zinc or other metal whose boiling-point is to be determined is shown at *k*. In this case a thermo-couple is used as a pyrometer, and it is inserted into the porcelain tube *d*. A reducing atmosphere of gas may be introduced through the tube *h*. The whole is enclosed in a Fletcher gas furnace, *F*. Gas enters through *A*, and the products of combustion escape at *D*.

The question naturally arises, how far may the indications afforded by the air-thermometer be trusted? Are the degrees

indicated by it, at a white-heat, comparable with the degrees of the ordinary thermometer? The author believes that there is no reason to expect exceptional deviations from Boyle's law at the high temperatures of ordinary furnaces; and, further, the evidence as to temperature indicated by the air-thermometer does not rest upon the expansion of a single gas; as the porcelain bulb may be filled with nitrogen, oxygen, or carbonic anhydride. The question as to the degree of confidence which may be reposed in the numerical values of high temperatures is, however, so important, that the author would refer to the following experiment of Carl Barus, who has devoted years of patient work to pyrometric investigations. Fig. 45a shows the arrangement adopted by him for comparing directly the air-thermometer with the thermo-junction.* The latter is inserted in a tubulure extending to the centre of the

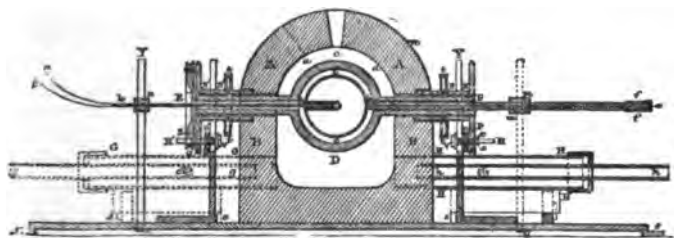


FIG. 45a.

bulb *e*; and the disposition of the various parts of the apparatus is as follows. The walls of a cylindrical furnace *B B* are covered with a hemispherical dome *A A*. The furnace is heated by gas, introduced through the burners *G G*, *H H*; compressed air entering by the inner tubes *g g* and *h h*. The inlets for the gas are *c c*. The furnace can be heated to a high temperature with ease; but in order to equalise the heat, Barus employs an internal globular "muffle," *E C D F*. It consists of two hemispheres of fire-clay, provided with lateral tubes, which pass through the walls of the furnace. The two hemispheres are held together by the iron collars *N N*, *N' N'*. The outer edges of these collars *P P'* are flanged, and fit into the grooves of two friction rollers, *Q Q'*, of which *R R'* are the respective axes. There are adjusting screws at *V V'*, *u u'*, *t t'*. The muffle is rotated by a belt pulley screwed on to the flange *P'*. The air-thermometer is shown in position,

* *Bulletin United States Geological Survey*, No. 54, Washington, 1889.

ffk i e, supported by the clamp *m m*. A similar clamp *n n*, on the opposite side of the furnace, supports the thermo-junction *k k*, the wires of which are shown at *a β*. It will be observed that the thermo-junction passes directly into the re-entering tubulure of the porcelain bulb; but the wires must not touch the walls of the tubulure. The capacity of the bulb *e* is about 300 c.c. The muffle is turned at the rate of about fifty revolutions per minute; and this speed, which is probably needlessly high, ensures uniformity in the temperature of the furnace.

It will be evident that the arrangements briefly described above enable the indications of the air-thermometer and the thermo-junction to be compared, and full details of the experiments will be found in the monograph by Barus. It will be found* that, if the results of the experiments be plotted with the electromotive force of the thermo-junction (in micro-volts) as abscissæ, and the temperatures, indicated by the air-thermometer, as ordinates, the several observations coincide very nearly with a straight line; and singularly valuable information is thus afforded as to the trustworthy character of the respective methods. The general conclusion would appear to be—that the thermo-junction, the use of which is very simple, may replace the air-thermometer, which, as arranged for accurate work, involves the employment of cumbersome apparatus and much tedious calculation; and is, in fact, about the last piece of apparatus that should be offered to engineers, with a view to the measurement of temperatures in the ordinary course of work.

An air-thermometer in a form adapted for industrial use has, however, been devised by Professor Wiborgh, of Stockholm,† who measures the pressure exerted by the expansion of a known volume of air, when forced into a porcelain bulb raised to the temperature which it is required to determine. Another form has recently been patented by Mr. H. L. Callendar;‡ who has so modified the differential air-thermometer as to enable the degrees of temperature to be read directly on a graduated tube.

* *Loc. cit.* p. 226.

† *Journal of the Iron and Steel Institute*, 1888, vol. ii. p. 110.

‡ *Proceedings of the Royal Society*, 1892, vol. i. p. 247.

OPTICAL PYROMETRY.

In conducting researches, the thermo-junction possesses, in the author's opinion, many advantages; but, unfortunately, its use involves appliances which are not sufficiently simple to be entrusted to ordinary workmen; and, as Professor le Chatelier has pointed out, the use of the thermo-electric pyrometer is only possible in works where the manager has a taste for scientific investigation, and devotes himself personally to it. In this country such cases are not rare, and the author would only cite, as an instance, the Clarence Works, where Sir Lowthian Bell has established a

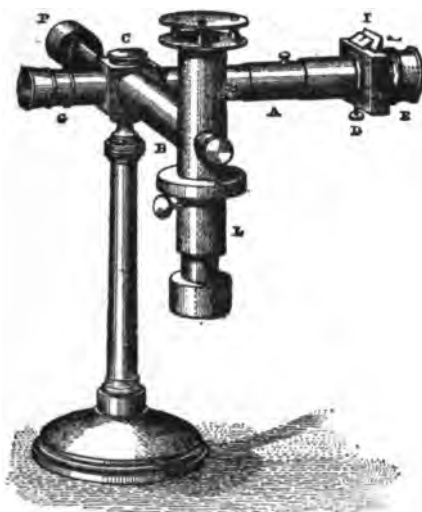


FIG. 45b.

system of electrical pyrometry in connection with the hot-blast mains; each of which may, in turn, be placed in pyrometric communication with a central office.

A less complicated but still trustworthy instrument of moderate accuracy was much needed; and le Chatelier has recently supplied one. The eye of the workman again becomes the pyrometer, but it is supplemented by an instrument which enables him to record the intensity of the radiations emitted by a glowing body; so that the old method of judging temperature by the appearance of the mass is rendered comparatively accurate, and

the familiar indications of "redness," "bright redness," and "whiteness," are subjected to direct measurement. Optical pyrometry is not new; but its history, which would include references to the honoured names of Pouillet, Ed. Becquerel, Crova, and Violle, is far too complex to be dealt with in this paper.

Mr. Crova* actually employed his spectro-pyrometer for industrial work, and measured the temperature of certain furnaces at the Creusot Works.

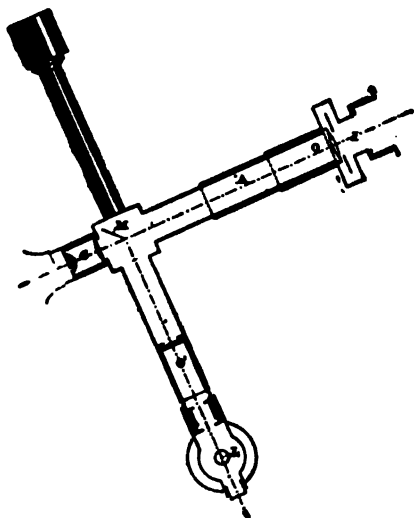


FIG. 45c.

Le Chatelier's† new photometric instrument is shown in Figs. 45b and 45c, and in its construction he has utilised the photometer of M. Cornu. The author is indebted either to le Chatelier's recently published papers, or to descriptions which he has furnished, for the details respecting the instrument which will now be given. The light, from a standard flame, or lamp L, burning amylic acetate, is reflected to the eye of the observer by the mirror M, while the light from the incandescent

* *Comptes Rendus*, vol. lxxxvii. 1878, pp. 322 and 979; *ibid.* vol. xc. 1880, p. 252; *ibid.* vol. xcii. 1881, pp. 36 and 707; *ibid.* vol. cxiv. 1892, p. 941.

† *Comptes Rendus*, vol. cxiv. 1892, p. 214; *L'Industrie Électrique*, No. 7, 1892, p. 147, where the formulæ given in this paper will be found.

body also passes to his eye through a red glass in the eye-piece G; this renders the radiations nearly monochromatic. There is an adjustable orifice at O, by which the amount of light admitted from the luminous body can be regulated. In order that intensities, which may often vary from 1 to 1,000,000, may be compared, absorbent glasses are employed; and these glasses are superposed at O' and E, in greater or less number, as may be necessary. P is a counterpoise, to equalise the weight of the other parts of the appliance. The luminous object, the temperature of which has to be determined, may be focussed by sliding the tube A'; and in order to measure the intensity of its radiations with this instrument, the procedure is as follows:—The position of the mirror M must be regulated by three screws at C, Fig. 6, so that the luminous image of the lamp, and that of the object to be measured, are brought into juxtaposition, being divided by the edge of the mirror.

The photometer depends upon the adjustment, to the same brightness, of two images; one being that of the flame of a standard lamp, and the other that of the object whose temperature is to be determined. The adjustment is made by means of a diaphragm formed of two plates, each with V-shaped notches opposite to one another. The two plates can be moved past one another by turning a milled head, D, and in this way a square aperture of variable size is formed; which, being placed in front of the object-glass O of the telescope, controls the amount of light admitted from the luminous object.

A divided scale I is attached to one half of the diaphragm, and a pointer to the other, and this gives directly a linear measurement n of the aperture.

Let n' be a measurement, when the image of an object of unit brightness (a candle-flame, for instance) is matched to that of the standard lamp; and n the measurement, when another object is matched in place of the candle. Since the eye-piece has a red glass within it, only red rays pass to the eye for measurement, and the intensity I , of these red rays emitted by the second object, as compared with those from the candle, will be given by the equation

$$I = \left(\frac{n'}{n}\right)^2.$$

But, if the two objects are not at equal distances from the instrument, the intensity will be apparently less for the more

distant one, in the ratio $\left(\frac{f}{f'}\right)^2$, where f and f' are the focal lengths (given on the tube A) of the two objects; hence—

$$I = \left(\frac{n'}{n}\right) \times \left(\frac{f}{f'}\right)^2.$$

As has been already stated, the great differences of intensity which have to be measured, occasionally render it necessary to absorb some of the rays from the object or from the standard lamp, as the case may be. This is done by inserting neutral-tinted glasses in suitable holders, either at E or F. Let N' be the linear measurement of the aperture, when the luminous object, shaded by a neutral-tinted glass, is matched with the standard lamp; and let N be a similar measurement when the same object is unshaded.

Then the coefficient of absorption of the glass, K , will be given by the equation

$$K = \left(\frac{N'}{N}\right)^2;$$

and, when p thicknesses of the neutral glass are before the object, whilst the standard glass is left unshaded,

$$I = \left(\frac{n'}{n}\right)^2 \left(\frac{f}{f'}\right)^2 \left(\frac{I}{K}\right)^p.$$

On the other hand, for measuring very low temperatures, when the standard lamp is shaded by p thicknesses of glass, and there are no glasses before the diaphragm, the formula becomes

$$I = \left(\frac{n}{n'}\right)^2 \left(\frac{f}{f'}\right)^2 K,$$

the index p being required because each glass cuts off a fraction of the light received by it.

Experiments indicate that the change in intensity of the red rays from a body of temperature T , is approximately given by the equation

$$I = 10^{6.7} T^{-\frac{3270}{T}},$$

where T is reckoned from absolute zero, so that $T = (t^\circ\text{C} + 273)$, t being the actual reading of the thermometer. This formula has been used to calculate the numbers given in the following Table—

Temperature. Centigrade.		Intensity of Red Rays.
600°	...	0.00008
800°	...	0.0046
1,000°	...	0.078
1,200°	...	0.64
1,400°	...	3.35
1,600°	...	12.9
1,800°	...	39.0
2,000°	...	93.0

the unit intensity being that of the axial zone of the flame of a standard candle.

In one instrument, where n' (the reading obtained with a candle flame as a luminous object) was 5.2, and $\frac{I}{K}$ had the value $\frac{1}{15}$, the following figures were obtained by Professor le Chatelier :

Temperature. Centigrade.	One Glass before Stan- dard Lamp.	No Neutral Glasses.	One Glass before Diaphragm.	Two Glasses before Diaphragm.
700°	39.5			
800°	15.2			
900°	7.4			
1,000°	3.8	19.2		
1,100°	—	10.8		
1,200°	—	6.7		
1,300°	—	4.2	21.2	
1,400°	—	2.7	13.8	
1,500°	—	—	10.1	
1,600°	—	—	7.4	
1,700°	—	—	5.6	
1,800°	—	—	4.3	21.5
1,900°	—	—	—	17.0
2,000°	—	—	—	13.8

But, inasmuch as the emissive power of different bodies for red rays is not the same under like conditions as to temperature, it will be doubtless preferable to calibrate the instrument directly by comparing it with a little mass of platinum, or of oxide of iron, which can be maintained at known temperatures as measured by a thermo-couple.

There is another optical instrument, the pyrometer devised by Messrs. Nonel and Mesuré, and used by the author for some years in the laboratory of the Royal School of Mines. It consists of a quartz plate A (Fig. 7) placed between two Nicol prisms; an

arrangement that renders it possible to suppress, at will, the radiations of any particular part of the spectrum, by simply rotating one of the Nicol prisms. If a hot body be observed through the instrument, and the prism be rotated by means of the divided head B, the red colour of the body will be seen to change to yellow, then to green, and finally to blue. The angle of rotation necessary to extinguish the red colour varies with the temperature, and serves as a measure of it; but the difficulty of remembering the precise tint by which the instrument was calibrated, prevents a high degree of accuracy from being attained in its use.

The importance of being able to measure high temperatures will now be considered with special reference to the work of the engineer. It is evident that the advantages of measuring and controlling the temperatures at which industrial operations are conducted, are more apparent on the metallurgical side of engi-

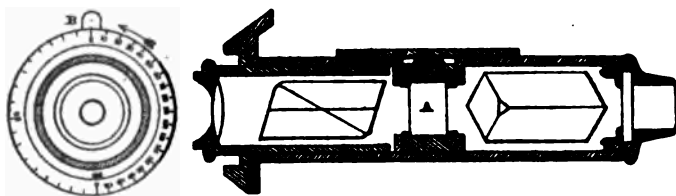


FIG. 7.

neering practice than on any other; but, apart from metallurgy, there are many problems in the solution of which pyrometry is of much service. The unaided eye, even of a trained and skilful workman, dealing with a special set of conditions with which he is familiar, is, probably, a far less trustworthy guide than it is often supposed to be; for, in estimating the temperature of a furnace, or that of a glowing mass of metal, much will depend upon the relative brightness of the illumination of the surrounding space. The author has had considerable experience in estimating the somewhat high temperatures of the "muffles," or little ovens used in the assay of gold and silver; but, on actually measuring, by means of the optical pyrometer, the temperature of two muffles in different positions in the same laboratory, he was surprised to find that they differed by more than 50° , although both appeared to be of nearly the same temperature.

Some measurements, made by the optical pyrometer, of temperatures employed in conducting industrial operations will now be given:

Gold Melting, Royal Mint.

	Centigrade.
Temperature of standard alloy, pouring into moulds . . .	1,180°
" " " (on a previous occasion, by thermo-couple) . . .	1,147°
Annealing 'blanks' for coinage, temperature of chamber . .	890°

Silver Melting, Royal Mint.

Temperature of standard alloy, pouring into mould . . .	980°
---	------

Open-Hearth Furnace, Woolwich Arsenal.

Hot gases in interior of melting chamber, about . . .	1,800°
Temperature of steel, 0.3 per cent. carbon :	
Pouring into ladle	1,700°
Pouring into moulds	1,700°
Pouring into moulds end of operation	1,650°

10-Ton Open-Hearth Furnace, Woolwich Arsenal.

Temperature of steel, 0.3 per cent. carbon, pouring into ladle	1,645°
Temperature of steel, 0.3 per cent. carbon, pouring into large mould	1,580°
Re-heating furnace, Woolwich Arsenal, temperature of interior	930°
Cupola furnace, temperature of No. 2, cast-iron pouring into ladle	1,600°

It is, of course, useless to attempt to deduce the temperature of a heated space, such as the interior of a re-heating furnace, from the radiations of an object which has been newly placed in it, and has therefore not had time to become thoroughly heated.

Professor le Chatelier* had previously measured the temperature attained in conducting some familiar operations; and, as the results obtained by him are, in the case of certain industries, entirely at variance with the estimations which have hitherto been made, it may be of interest to quote a few of them :

Bessemer Converter (6 Tons Capacity).

	Centigrade.
Pouring the slag	1,580°
" " steel into ladle	1,640°
" " into mould	1,580°
Re-heating furnace	1,200°
Ingot under the hammer	1,080°

* *Comptes Rendus*, vol. cxiv. 1892, p. 470.

Siemens-Martin Open-Hearth Furnace.

[illegible]

Regenerative Furnace for Crucible Steel.

Temperature in the spaces between the crucibles . . . 1,600°

Blast Furnace, Smelting Grey Pig.

Opening in front of the "tuyere"	1,930°
Tapping the pig-iron	beginning 1,400°
	end 1,570°

Siemens Furnace, used for Melting Glass.

Furnace	1,400°
Furnace for hard porcelain, end of the "baking"	1,370°
Hoffmann kiln (brick-burning)	1,100°
Temperature of incandescent electric lamps from	1,800° to 2,100°

GENERAL CONSIDERATIONS.

The accurate measurement of high temperatures is increasing in interest, in view of the rapid development of the study of chemical dynamics. It is now recognised that the industrial chemist, as well as the engineer, has to deal with the influence of mass. Many chemical processes are reciprocating, so that the original product may be obtained from the product of the reaction. The result of such opposed processes is a state of chemical equilibrium, in which the original and the newly formed substances are present in definite quantities; and remain the same so long as the conditions, more especially those of temperature and pressure, do not undergo further change. In conducting many operations, temperature and pressure are reciprocal factors; hence the importance of being able to measure with accuracy a bright red heat. Now, as Professor le Chatelier has already pointed out, in the production of chlorine by the Deacon process, or in

the baking of porcelain, a variation of temperature of only 20° may be attended with complete failure of the operation. There is, however, one other case of more direct interest to the engineer, in relation to steel. It involves the consideration of the possibility of the occurrence, at high temperatures, of molecular changes in steel, which profoundly modify its mechanical properties, in a way that is further indicated on p. 121. It is difficult to describe briefly the nature of this change, but the following statement may be sufficient.

When a mass of steel is cooled from a very bright red heat, say from 1200° Centigrade to the ordinary temperature of the atmosphere, at least three critical points, each attended by an evolution of heat, may be detected by the pyrometric methods already indicated; and their position may be determined very precisely by the aid of the autographic method already described and illustrated. The development of the theory of the importance of these critical points is mainly due to Osmond,* who has fixed the normal temperatures at which they occur during the slow cooling of a mass of steel in which the notation of Chernoff and of Osmond has been retained.

The author has already stated his belief that these changes are of great importance in modifying the structure, and consequently the mechanical properties, of steel; and he is fortunate in sharing this opinion with Dr. Anderson, the Director-General of Ordnance Factories, who is instituting, at Woolwich Arsenal, some interesting experiments bearing on the question. The initial temperature of the mass, and its rate of cooling, are not without influence on the temperatures at which these critical points occur. For instance, in hardening large pieces of steel, such as the "A" tubes of guns, it may happen that, when the mass is plunged into the oil bath, a portion of the metal may be at a temperature below that at which the molecular transformations occur. In large masses of steel, the bath may exert a "hardening" action on the hot interior of the mass of steel, and none at all on the cooler surface. It is, moreover, only necessary for the temperature of different parts of the mass to vary within a narrow range, in order that the bath may exert different influences on adjacent parts of the steel. This is a matter of great importance, and M. Barba of the

* See Report by the Author to the Alloys Research Committee of the Institution of Mechanical Engineers. *Proceedings*, No. 5, 1891, p. 543, and *Nature*, vol. xli. 1889, pp. 11, 32, where references are given to Osmond's Papers.

Creusot Works began its study in 1880, but abandoned the attempt for want of sufficiently exact and practical methods of measuring high temperatures. The author attacked the problem in 1891, and published the results of the only experiment which had then been made. For the purpose of conducting it, Dr. Anderson caused an ingot of steel to be prepared, 8 inches high and 4 inches in diameter. It contained carbon 0.799, silicon 0.084, manganese 0.412. A *le Chatelier* thermo-junction was placed in a hole drilled to the centre of the mass, and another thermo-junction was fixed in a hole drilled near the surface. The mass was heated to bright redness, the external junction indicating 1100° Centigrade, each thermo-junction being in turn switched into connection with the recording apparatus, Fig. 4; and dotted curves representing the cooling of the exterior and at the interior of the mass were thus obtained. The cooling was effected by plunging the mass into water. The effect of rapid cooling on the surface was, of course, to contract it and to compress the mass; the pressure being very marked in the zone of the ingot in which the external thermo-junction was inserted. The result appeared to be a lowering of the critical point (which should have occurred at about 660° Centigrade) to a little over 400° Centigrade.

It would therefore appear that the great problems of chemical equilibrium are applicable to the relations between the constituents of the complex material, steel; and that the pressure exerted on the molecules of a metallic mass must be measured, as well as its temperature, in investigating the molecular grouping of metals, upon which their mechanical properties depend.

It may now be well to indicate very briefly some other directions in which the measurement of high temperatures may be useful. The spent gases from boiler-furnaces are often hotter than 400°, and their temperature should, in many cases, be accurately known. In researches on heat-engines, complex problems arise demanding a knowledge of temperatures of about 500°. Foundry practice presents numerous cases, as, for instance, casting guns by the Rodman system; in conducting which it is most important, as Mr. H. B. Howe, of Boston, has pointed out, to be able to measure and control the rate of cooling of the core of the gun, as compared with its outside. By this means, it is possible to avoid setting up prejudicial stresses, and to promote the development of useful ones in castings of all kinds. Mr. George Addy has appealed to the importance of pyrometry, in connection with experiments on armour-piercing projectiles; and it will be evident that the use of projectiles and explosives is a branch of engineer-

ing fertile in problems, the solution of which must, in a great measure, be based on pyrometry.

The gradual introduction of new alloys is changing the methods of investigation which must precede and govern the use of materials in construction. It may be thought that work of the kind indicated in this chapter is not sufficiently practical to deserve the attention of either the metallurgist or the engineer. If fears of this kind should arise, the author would recall the eloquent words recently addressed by the Director-General of Ordnance Factories to such doubters, who, he says, "can never have been placed in positions of responsibility, where the safety of ships, the lives of their passengers and crews, the efficiency of armaments, and their own financial position were in question; they can never have looked at masses of steel, with the view of deciding whether they were fitted for the purpose for which they had been produced; nor can they ever have felt the helplessness, and the want of reasonably secure guidance, which it is still the lot of the responsible judge to experience." The guidance for which Dr. Anderson appealed can only be afforded by employing to the fullest extent, the methods, as well as the results, of physical and metallurgical research.

Experimental Pyrometric Work.—It may be well, in concluding this section of the book, to describe certain experiments, recently made by the author* with the aid of the thermo-junction, which shows what good service the instrument may be expected to render in the future. The student will bear in mind that if an ordinary thermometer be plunged into water which is gradually losing heat to a cold environment, the mercury will fall until the water begins to freeze, but directly this happens the mercury will remain stationary until all the water is frozen; so that if the rate of fall be measured with a chronograph there will be a steady fall to the freezing point of water, then a long arrest followed by a renewed fall. If these readings are plotted a well-known time-temperature curve will be obtained. Exactly the same effect is produced when a fluid metal "freezes," and if the thermo-junction, suitably protected by a thin layer of fire-clay, or, in certain cases, by a very thin tube of glass, be placed in the mass of fluid metal, the point at which the mass freezes may readily be ascertained and recorded by the photographic method described on page 151, Fig. 44*d*.

A mass of gold having an initial temperature of about 1250° C., is allowed to cool to 1045° C. when the mass begins

* *Proc. Roy. Soc.*, vol. xlix. 1891, p. 347.

to solidify. The curve is approximately horizontal during solidification, and throughout its entire course appears to be a perfectly normal curve of a cooling mass of metal, no points of exceptional absorption or evolution of heat, such as would occur in iron, being observable.

The curve obtained in a similar way, and representing the cooling of gold with 0.5 per cent. of lead, is like the one representing the cooling of pure gold, but it will be evident that the presence of lead lowers the freezing point of gold by an amount which is found by measurement to be about $7^{\circ}.5$ C.

A very different molecular condition is, however, established by the presence of aluminium. With 0.47 per cent. of this element the true freezing point can be detected, but is nearly obliterated, and the mass does not become truly solid until the temperature has fallen to 900° C.

It is of interest to ascertain how far the lowering of the freezing point of gold is in accordance with the results of Raoult's investigations on the lowering of the freezing point of solutions. His generalisations have been tested in the case of solutions of metals in metals with low melting points (tin, lead, and bismuth), in an admirable series of experiments by Heycock and Neville.* In order to calculate the lowering of the freezing point of gold produced by one atom of the added element to 100 atoms of the solvent, which has been the usual method of stating such results, it is necessary to know the latent heat of fusion of gold, and this had not been determined, probably because the accurate measurement of the latent and specific heats of metals with high melting points, such as gold, presents many more difficulties than the determinations of similar constants for bodies having low melting points.

Viollet† found the specific heat of platinum at different temperatures by heating a piece of the metal in a specially constructed muffle, the temperature being simultaneously determined by means of a porcelain air-thermometer. The temperature of the metal being known, he plunged it into a calorimeter, and calculated from the data he obtained the mean specific heat of platinum between the extreme temperatures of the experiment. By making many experiments at different temperatures, he was able to deduce the specific heat of platinum at any point within the range, and he found that it regularly increased with the temperature. The data thus afforded

* *Journ. Chem. Soc.*, vol. lv. 1889, p. 666; vol. lvii. 1890, pp. 376 and 656.

† *Comptes Rendus*, vol. lxxv. 1877, pp. 543-546.

enabled him to obtain the freezing point of platinum by transferring metal just *after* solidification into the calorimeter. Further, by pouring metal just *before* its solidification into water, it was easy to determine the total amount of heat evolved during cooling. Hence, knowing the amount of heat evolved by the mass after it had become solid, and deducting this amount from the total heat transferred to the water by the melted platinum, he obtained the latent heat of fusion of the metal.

He also determined* the specific heat and melting point (1045°C.) in the case of gold, but he does not appear to have ascertained what is the latent heat of fusion of the precious metal. The following experiments were therefore made by the author† in order to afford a basis for calculating the theoretical lowering of the freezing point of gold which a given addition of impurity should produce.

A calorimeter of polished silver, 10.5 cm. diameter, and 15.5 cm. high, was supported upon three points of cork within a bright metallic vessel, blackened externally, and constituting an air-jacket. The amount of water employed varied from 800 to 1088 grams. The stirrer was a thin sheet of mica, mounted upon a silver wire, bent at its lower end into the form of a hoop; the mica also served to catch the gold poured into the water. Quantities of very pure gold, varying from 68 to 123 grams, were melted in a small clay crucible and poured into the calorimeter.

In experiments A and B and E to I, the temperature of the molten mass was measured, by the aid of the thermo-junction previously described, which was placed directly in the molten gold, up to the moment of pouring, and it is believed that the temperature of the mass was known to within 2°C.

At the end of each experiment, the gold poured into the calorimeter was carefully collected and weighed. The thermometer used was a very sensitive one with fixed zero, and it could easily be read to 0.02°C. The depth of water employed was sufficient to prevent the evolution of steam, and none was observed to escape in any of the experiments recorded.

The calculations are as follows:

Let P = weight of water in calorimeter.

p_1c_1 = water equivalent of calorimeter.

p_2c_2 = " " thermometer.

p = weight of gold employed.

* *Comptes Rendus*, vol. lxxxix. 1879, pp. 702, 703; xcil. 1881, pp. 866-8.

† *Proc. Roy. Soc.*, vol. xlix. 1891, p. 347.

c = average specific heat of gold (Violle).
 t = initial temperature of the molten gold.
 T = " " " " water.
 t_1 = final temperature of the water.

The total quantity of heat carried to the calorimeter by p grams of gold consists of the amount of heat which was required to raise the temperature of the metal to its melting point, *plus* the amount actually required to melt it; or

$$(P + p_1c_1 + p_2c_2)(t_1 - T) = pc(t - t_1) + p\lambda,$$

where λ is the latent heat of fusion of gold required;

$$\therefore \lambda = \frac{(P + p_1c_1 + p_2c_2)(t_1 - T) - pc(t - t_1)}{p}$$

Taking, therefore, 16.3 as the latent heat of fusion of gold, and proceeding to find the lowering $\delta\theta$ of the freezing point, due to the presence of an impurity,

$$\delta\theta = \frac{\theta\omega}{\lambda\rho},$$

where

θ = freezing point of gold, from absolute zero,
 ω = osmotic pressure in dynes,
 ρ = density of the solvent,
 λ = latent heat of fusion of the solvent in dynes.

Inserting values

$$\begin{aligned}
 \delta\theta &= \frac{1040 + 273}{1} \times \frac{(1013 \times 10^8 \times 22.3 \times 1300)}{19.6 \times 273} \rho \\
 &= \frac{1313 \times 1013 \times 22.3 \times 1300}{19.6 \times 16.3 \times 41.6 \times 10^8 \times 273} \\
 &= 10^{-6} \text{ C.}
 \end{aligned}$$

Experiments are in progress with a view to ascertain whether the mean specific heat of very pure gold is the same as that found by Violle, for there is every reason to believe that the presence of impurity has great influence upon this constant. A few measurements already made would seem to indicate that his result is low, and this is important, because a slight difference in the specific heat will have a material effect upon the latent heat of fusion, and consequently on the theoretical atomic fall in the

Table of Experiments. In Centigrade-gramme Units.

	P	P ₀₁	P ₀₂	P*	e.	t.	T.	t ₁	λ.	Remarks.
A.	800.75	15.42	0.86	84.72	0.0352 Violette	1075*	13.4	19.0	16.83	Solidification had just begun.
B.	800.75	15.42	0.86	68.68		1050*	12.9	17.4	17.07	
C.	933.1	15.72	1.16	87.11		1045	9.68	14.52	16.51	
D.	808.7	15.72	1.16	76.05		1045	10.34	15.18	16.29	
E.	1088.6	16.37	1.16	119.6		1045*	11.79	17.47	16.36	
F.	1088.6	16.37	1.16	123.0		1045*	11.74	17.50	15.62	{ 16.38. Mean of the nine experiments.
G.	1088.6	16.37	1.16	79.19		1045*	12.11	15.88	16.43	
H.	1088.6	16.37	1.16	105.05		1085*	13.52	18.61	16.05	
I.	1088.6	16.37	1.16	102.75		1070*	14.30	19.21	15.87	

* These temperatures were measured by the aid of the pyrometer, and, as the metal was slightly above its melting point, it was necessary to assume that the specific heat of the fluid gold is practically the same as that of solid gold near its melting point. The slope of the autographic curves, moreover, shows that any error so introduced would be but small.

freezing point produced by aluminium. In order to ascertain whether aluminium would give the normal lowering of the freezing point ($10^{\circ}.6$ for each atom present in 100 atoms of gold) a crucible, fitted with a tubulure, as already described, was taken, and 130 grams of very pure gold was melted in it. The crucible was then placed over the thermo-junction, and allowed to cool, the freezing point of the metal it contained being recorded in the usual way by a curve. The gold was then re-melted, and a weighed quantity of aluminium added, the mass being stirred and the temperature of its freezing point measured and recorded in a curve.

The addition of 0.2 per cent. of aluminium produced an appreciable fall in the freezing point, but this initial fall is only indicated by a change in direction of the curve. The fall as measured upon the photographic plate is only 1 mm., which nevertheless corresponds to a difference of temperature of $7^{\circ}.68$ C.

A further addition of 0.2 per cent. of aluminium (making 0.4 per cent.) increased the fall to 1.8 mm., corresponding to $14^{\circ}.28$ C. It may be urged that these measurements are small, but the observations were repeated with a scale some distance from the galvanometer, and chronographic records gave results having the same values.

An experiment with gold in which 1 per cent. of aluminium was present also confirms this; the fall in temperature of the freezing point was in this case $33^{\circ}.66$ C., but there were indications that the gold, the solvent, was becoming saturated.

Now 0.2 per cent. of aluminium corresponds to $2/10 \times 196/27.5 = 1.42$ atom per 100 atoms of gold.*

Hence the fall per atom present per hundred atoms of gold = $7.68/1.42 = 5^{\circ}.4$ C.

Similarly, a percentage of 0.4 corresponds to $4/10 \times 196/27.5 = 2.85$ atoms per hundred of gold, and the fall per atom = $14.28/2.85 = 5^{\circ}.0$ C.

With 1 per cent. of aluminium the total fall will be due to 7.16 atoms per hundred of gold; hence the atomic fall will be $33.66/7.16 = 4^{\circ}.7$ C.

It may be added that experiments (as yet incomplete) seem to show that lead, bismuth, silicon; and platinum cause a much greater "atomic fall" in the freezing point of gold than aluminium does.

The relations of aluminium to gold would, therefore, appear to be peculiar in more ways than one. The curve (Fig. 3) clearly

* 196 is the atomic weight of gold, 27.5 that of aluminium.

indicates that aluminium has a remarkable influence on the cooling of a mass of gold, and in view of this it would seem strange that calculations based on the atomic weight of aluminium should show that it delays the *initial* solidification of gold less than other elements. The *complete* solidification is, however, much retarded; for merely stirring a mass of gold contaminated with very little aluminium reveals the fact that the added element has set up during the solidification of the mass a "pasty stage" which continues through an unusually long range of temperature.

In the metallurgy of iron, aluminium is known to play an important part, and the introduction of a small quantity of it renders it possible to cast very mild steel or even "wrought" iron into forms which are remarkable for delicacy and soundness. The mode of action of the aluminium on iron in the "mitis castings" has given rise to wide divergence of opinion, but the view that it acts by the removal of oxide, or of occluded oxygen, has gained much favour. In the case of gold, which has neither occluded oxygen nor oxide to lose, the castings of the metal with 0.2 per cent. of aluminium are also remarkably sound, and, as experiments prove, very tenacious; the action of the aluminium is, therefore, probably a molecular one of much complexity.

It may be pointed out that the presence in gold of quantities of silver which vary from 0.1 to 4.0 per cent. does not lower the freezing point of the mass. Messrs. Heycock and Neville, who witnessed certain of the experiments above described, inform me of the hitherto unpublished fact, observed by them, that the presence of thallium does not lower the freezing point of lead.

The close concordance in both these cases between the atomic volumes of the mass of metal and the added impurity is of special interest in connection with the generalisation given in another chapter. Silver has the same atomic volume as gold, and if present in small quantity, produces no effect on either its tenacity or its freezing point.

Throughout these experiments gold was simply employed for the sake of its freedom from liability to oxidation, but other metals must be studied, and it is worthy of record that Hadfield has recently shown that the parts played by aluminium and by silicon in steel are almost identical. Most of the physical properties of aluminium and silicon, in a free state, are totally different, but they possess the same atomic volume, and when they are alloyed with iron they affect it in precisely the same way.

The author in 1891 described and exhibited to the Royal Society a new alloy of gold and aluminium, AuAl_3 , which is remarkable for its intense purple colour.

The gold-aluminium alloys were found to have one interesting peculiarity which deserves special mention. The addition of 0.2 per cent. of aluminium to gold produces an appreciable fall in the freezing point, an addition of 0.4 per cent. causing a fall of $14^{\circ}.28$, or an "atomic fall" of $5^{\circ}.0$ C.

These facts indicated that it was desirable to ascertain what are the melting points of the gold-aluminium series of alloys generally, and this has now been done with the aid of the Le Chatelier thermo-couple, used in the way which was previously described.

The results show that, although a white alloy, containing 10 per cent. of aluminium, has a melting point which is no less than 417° lower than that of gold; the purple alloy, on the other hand, melts at a point which has yet to be definitely fixed, but which is several degrees above gold. In fact, when workmen who are accustomed to melt gold on a large scale, attempt to melt this purple substance, they find it difficult to believe that they are dealing with a gold alloy, as it is so intractable.

The melting points of the rest of the series richer in aluminium, appear to fall continuously to 660° , a little below the melting point of aluminium (665° C.). These melting points of the aluminium-gold series of alloys have been plotted in a diagram,* which also shows the tenacity and density of the various members of the series.

The purple alloy presents a singular case of an alloy, free from mercury, having a higher melting point than that of the least fusible of its constituents, and this fact affords strong evidence of its being a true compound of gold and aluminium.

It is generally admitted that there are true compounds in the copper-tin series, for SnCu_3 and SnCu_4 seem to be well defined, but their melting points are much lower than that of copper.

A. P. Laurie† has shown that in the gold-tin series, the alloy containing 63 per cent. of gold and 37 per cent. of tin has an electromotive force which distinguishes it from the rest of the series, and points conclusively to its being a true compound, but the author finds that it melts readily below redness.

The melting points of ordinary chemical compounds are often much higher than the melting point of the least fusible constituent. *Galena*, for instance, melts at a strong red heat; it is difficult to fix the point accurately as the substance volatilises, but it is close to 900° C. Its constituents, lead and sulphur, melt at 326° and 115° respectively. *Stibnite* also, sulphide of

* *Nature*, vol. xlv. 1892, p. 539.

† *Phil. Mag.*, vol. xxxiii. 1892, p. 94.

antimony, melts at about 530° , according to Dr. Joly, while antimony fuses at 440° .

The method of taking autographic curves of cooling masses of fluid metal ought to enable much information to be gained as to what is taking place throughout the mass. Such curves should render it possible to ascertain which of the rival theories as to the nature of solution, as applied to salts, is supported by the behaviour of a metal dissolved in a metal. When, for instance, a little aluminium dissolves in gold, is the analogue of a hydride formed, and, if so, is the curve of freezing points of a series of aluminium-gold alloys a continuous one? On the other hand, does the theory advocated by Van 't Hoff, Arrhenius, and Ostwald gain support, and do the molecules of the dissolved metals act independently of the solvent—that is, does osmotic pressure come into play? It will be remembered that the law which regulates osmotic pressure has exactly the same form as Boyle's law—that is, the pressure is proportional to the density of the gas or of the solution. Is the view of Arrhenius correct—that, if a solution be very dilute, the molecules of the dissolved substance are dissociated, act independently of each other, and behave like a perfect gas?

It will require years of patient work before these questions can be answered; but it appears certain, from the admirable experiments of Heycock and Neville,* to which reference has already been made, that, taking metals with low melting points (such as tin or lead) as solvents, the lowering of the freezing point of the solvent is really due to the bombardment exerted by the molecules of the dissolved metals.

There is yet one other question: When metals are added in small quantities to a metallic mass, may the solvent remain inert? Take a mass of 1000 grams of lead, add to it 15 grams of gold, or 16 atoms for every 100 atoms of lead. It could be shown that the gold is readily dissolved, and remains dissolved, even if the lead be solidified. Now, if to the fluid lead sufficient aluminium be added to form the purple alloy with the dissolved gold, and the mass be well stirred, the aluminium will not unite with the lead; it will nevertheless find out the gold and, after uniting with it, will carry it to the surface of the bath. Thence it can be removed, and the alloy identified by its purple colour.

The union of the aluminium and the gold must, however, be peculiar. Crookes has shown that when this alloy is used as an electrode in a vacuum tube, the gold is volatilised from the alloy and deposited as a film on the glass, leaving the aluminium behind.

* *Loc. cit.*

The purple alloy presents us with the most interesting case yet known of a molecule built up of purely metallic atoms, but we are certain that the atoms are still those of gold and aluminium—that is, the atoms of the united metals remain unchanged. The interest in this substance is deepened if it be remembered that our aim at the present day is the same as that of the alchemists, for we are striving, as they did, to attack and change the chemist's atoms themselves. We seek, as truly as they, to effect the transmutations, which, as Boyle said, would “be none the less real for not being gainful,” and employ high temperatures in the hope of simplifying the molecular structure of metals. We no longer consider gold to be the “sum of perfection,” but still retain the belief expressed by Geber, eleven hundred years ago, that “if we would change metals, we must needs use excess of heat.” A poet also appears to have felt this, for George Herbert quaintly writes in the seventeenth century—

“I know . . . what the stars conspire,
What willing Nature speaks, what forced by fire ;”

thus comparing the ordinary response of Nature to the investigator with the evidence he elicits from her by heat.

By fusing gold, and staining it “the purple of the dawn,” a new interest has been given to the metal which the alchemist always connected with the sun; and for further proof that metallic atoms may be changed, we must turn to the sun itself, as to a great metallurgical centre, where “all the elements shall melt with fervent heat.”

I. NATURAL FUELS.

1. **Wood.**—When dry, wood consists of 96 per cent. of woody tissue (cellulose, $C_6H_{10}O_4$) and 4 per cent. of sap. A small proportion of inorganic matter is also present, and, when recently felled, all wood contains a large proportion of water. The mean composition of well-dried wood is—

Carbon.		Hydrogen.		Oxygen.		Nitrogen.
50.0	...	6.0	...	42.0	...	2.0

or, roughly, 50 per cent. of carbon and 50 per cent. of chemically combined water. Air-dried wood contains 40 per cent. of carbon, 40 per cent. of chemically combined water, and 20 per cent. of hygroscopic water. The proportion of ash-giving constituents varies from 1.2 to 2.3 per cent., the average percentage being 1.5. The ash consists of about 70 per cent. of calcium carbonate, 20 per cent. of alkaline carbonates, together with varying amounts

of alkaline sulphates and chlorides, silica, phosphoric anhydride, magnesia, ferric oxide, manganous oxide, and alumina. The specific gravity of wood varies considerably. Air-dried woods, with 20 per cent. of moisture, having a specific gravity of more than 0.55, are classed as *hard*; with a lower specific gravity they are classed as *soft*. After the air has been completely expelled from the pores of the wood, the specific gravity is in all cases nearly the same, varying only from 1.48 to 1.53. The calorific intensity of wood is small, but its combustibility and the amount of flame it gives are very great. The large percentage of hygroscopic water renders wood unsuitable as a fuel in cases where high temperatures are required, and the rapid demolition of forests tends to increase its cost.

2. *Peat*.—Peat or turf is the product of the slow decay of plants under conditions in which the supply of air is limited. It is formed chiefly from the mosses *Sphagnum* and *Hypnum*, with other plants. It may be classed, according to the localities where it has been produced, as highland and lowland peat, according to its age as recent peat, and as old peat with only traces of organic texture, and, lastly, according to the mode in which it has been extracted, as "cut peat" or "dredge peat."

Peat deposits are widely distributed throughout the world. In Ireland it is estimated that the peat area is not less than one-seventh of the island. That of Great Britain covers six million acres, with an average depth of 12 feet. Extensive deposits are met with in Russia, where peat is of metallurgical importance, in North Germany, Austria, and Scandinavia.

The composition of peat is extremely variable, the proportion of water and of ash-giving constituents having so great an influence that it is almost impossible to estimate its average composition. The best air-dried peat still contains 25 per cent. of hygroscopic water. From numerous analyses, the composition of pure peat, exclusive of moisture, has been found to be as follows:—

Carbon.	Hydrogen.	Oxygen.	Nitrogen.
49.6 to 63.9 ...	4.7 to 6.8 ...	28.6 to 44.1 ...	0.0 to 2.6

in which the ratio of the oxygen (with the nitrogen) to the hydrogen is as 5 or 6 : 1.

The mean composition of good air-dried peat is approximately—

Hygroscopic Water.	Water.	Hydrogen.	Carbon.
25.0 ...	28.5 ...	1.5 ...	45.0

The proportion of ash-giving constituents, however, varies from

1 to 30 per cent. and more, being rarely below 10 per cent. The ash consists chiefly of lime, ferric oxide, and silica, together with phosphoric acid, sulphuric acid, and carbonic acid, and, in considerable quantities, alkalies, alumina, and magnesia. Raw peat also frequently contains iron pyrites. The high percentage of ash and of water, together with its bulk, are the main objections to the use of peat as fuel. For an equal evaporative power, its bulk is from 8 to 18 times that of coal.

Numerous methods have been adopted for freeing peat from ash and moisture. They consist chiefly in the subdivision of the peat into minute fragments. These are washed, and dried, with or without compression.

The calorific power of peat varies inversely as the amount of water and ash it contains. For peat without ash and water, the calorific power is 5237, whilst for ordinary air-dried peat it does not exceed 3000.

The specific gravity of peat varies, with the proportion of ash and the mode of preparation, from 0.113 to 1.039.

3. *Lignite*.—Brown-coal and lignite occupy an intermediate place between peat and true coals, there being no abrupt break in the compositions. Indeed, the transition from woody tissue to anthracite is gradual, as is well shown by the following tabular statement, in which the carbon is represented as a constant quantity:—

	Carbon.	Hydrogen.	Oxygen.
Wood	100	12.18	83.07
Peat	100	9.85	55.67
Lignite	100	8.37	42.42
Bituminous coal	100	6.12	21.23
Anthracite	100	2.84	1.74

(Percy.)

The term lignite is used by British and American writers as synonymous with the brown-coal of the Germans. It is usually applied to those varieties of coal which are older than peat and more recent than the coals of carboniferous age. Many writers, however, erroneously confine the term lignite or brown-coal to coals of the Tertiary epoch. Four fairly distinct types of lignite may be distinguished—(1) Fossil wood, fibrous brown-coal, the lignite of the Germans, which has a distinct ligneous texture; (2) Earthy lignite, without structure and earthy in fracture; (3) Conchoidal lignite, without any distinct vegetable structure and

with a conchoidal fracture; (4) Bituminous lignite, a black shiny fuel sometimes resembling anthracite, and having a conchoidal or earthy fracture. For metallurgical purposes, the first three types only are of importance, the fourth type being used more frequently as material for the production of tar than as a fuel.

When recently raised from the mine, lignites contain as much as 33 per cent. of moisture, and even more. When air dried, however, they lose half this amount. The proportion of ash varies from 3 to 30 per cent. The ash contains lime, alumina, and silica, together with magnesia, some alkalies, and ferric oxide, and an appreciable quantity of sulphuric acid, but as a rule no phosphoric acid. The mean percentage composition of lignite is as follows:—

Variety.	Carbon.	Hydrogen.	Oxygen.
1. Fibrous . . .	57 to 67	5 to 6	28 to 37
2. Earthy . . .	45 to 70	5 to 6	25 to 30
3. Conchoidal . .	65 to 75	4 to 6	21 to 29
4. Bituminous . .	70 to 80	6 to 8	12 to 24

Lignite burns with a long smoky flame. The calorific power varies considerably, the mean calorific power of the four varieties being—(1) 5000, (2) 5700, (3) 6500, and (4) 7000 *calories* respectively. The value of lignite as fuel would thus appear to be considerable, but in practice complete desiccation is hardly attainable, and a high percentage of moisture is always retained. The only practical method of increasing the calorific power of lignite is by removing this moisture, and for this purpose drying in air, heating in kilns, or compression has been attempted with considerable success.*

4. Coal.—Coals, formed previously to the Cretaceous period, are distinguished from lignites by their deep-black streak, great density, and friability. The fracture is more lamellar, the ligneous texture having disappeared. When subjected to dry distillation, they yield a greater amount of carbonaceous residue, and the condensed products contain less water than is the case with fuels of more recent age. Coals contain very little water, and when dried at 100° they are considerably less hygroscopic than wood and lignite. The specific gravity of pure coal, with a low percentage of ash, varies from 1.2 to 1.4, the density being in direct proportion to the percentage of carbon. A cubic yard of coal averages

* Zincken, *Physiographie der Braunkohle*, Hanover, 1867–71.

18 cwt. in weight. The proportion of coke left on distillation varies from 50 to 90 per cent., and the composition of coal varies within the following limits:—

Carbon.		Hydrogen.		Oxygen.
75 to 93	...	6 to 4	...	19 to 3

With the oxygen is included 1 to 2 per cent. of nitrogen. In coals the ratio of the oxygen (with the nitrogen) to the hydrogen varies between the wide limits of 1 : 1 to 4 : 1.

Coals may be classified according to the length of the flame, and the character of the residue which is left when they are subjected to dry distillation. The old classification, based solely on the character of the coke produced, divided coals into two classes, *caking* and *non-caking*, according as the coke produced formed a compact or pulverulent mass. Percy classed coal into three varieties—(1) non-caking or free-burning, rich in oxygen; (2) caking; (3) non-caking, rich in carbon. This classification is based on the chemical composition of the coals, and therefore on their calorific power. Gruner was led to adopt a more detailed classification, in which five types are distinguished—

(1) *Non-caking Coals with Long Flames*.—These coals, which most closely approach lignites, when subjected to dry distillation yield 55 to 60 per cent. of pulverulent coke, the evolution of volatile gases giving rise to a long smoky flame. The composition varies within the following limits:—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
75 to 80	...	4.5 to 5.5	...	15.0 to 19.5

the ratio of the oxygen to the hydrogen being 3 : 1, or 4 : 1. The calorific power generally varies from 8000 to 8500, and the evaporative factor, or number of times its weight of water evaporated by a unit weight of coal from 8 to 10. Coals of this type are of common occurrence in Scotland, Derbyshire, and Staffordshire.

(2) *Caking, Long-flame Gas-coal*.—Coals of this type contain:—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
80 to 85	...	5 to 5.8	...	10 to 14.2

the ratio of the oxygen to the hydrogen being 2 : 1, or 3 : 1. They yield on slow distillation 60 to 68 per cent. of caked, but very friable and porous, coke, and 32 to 40 per cent. of volatile matter, of which 17 to 20 per cent. is gas. The calorific power generally varies from 8500 to 8800, and the evaporative factor from 8 to 9.7.

(3) *Bituminous or Furnace Coal*.—These coals are black, not

very hard; they burn with a smoky flame, at the same time softening and intumescing in the fire. They contain—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
84 to 89	...	5 to 5.5	...	5.5 to 11

the ratio of the oxygen to the hydrogen being 1:1. They yield 68 to 74 per cent. of caked and swollen coke, and 15 to 16 per cent. of gas. The calorific power varies from 8800 to 9300 and the evaporative factor from 9.7 to 11.

(4) *Caking Coals with Short Flame.*—These contain—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
88 to 91	...	4.5 to 5.5	...	5.5 to 6.5

the ratio of the oxygen to the hydrogen being 1:1. They yield 74 to 82 per cent. of caked and very compact coke, and 12 to 15 per cent. of gas. The calorific power varies from 9300 to 9600 and the evaporative factor from 11 to 12.

(5) *Anthracitic Coals.*—These burn with a short flame, and have the following composition:—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
90 to 93	...	4 to 4.5	...	3 to 5.5

the ratio of the oxygen to the hydrogen being 0.5:1. These coals form the transition to true anthracites. On coking, they yield 82 to 92 per cent. of pulverulent or fritted coke, and 12 to 18 per cent. of gases. The calorific power varies from 9200 to 9500, and the evaporative factor from 10.8 to 11.4. Coals of this type are met with in South Wales and in Pennsylvania.

The percentage of ash yielded by the several varieties of coal ranges from 1 to 30, but seldom exceeds 7. The ash consists mainly of silica, with alumina, lime, magnesia, ferric oxide, and manganic oxide. Sulphuric acid is also frequently present; but the proportion of phosphoric acid is usually inconsiderable.

5. *Anthracite.*—This is the ultimate product of the conversion of vegetable matter into coal. Its colour is jet black, with a vitreous lustre; its structure homogeneous, and its fracture conchoidal.

The mean of a large number of analyses gave the following as the composition of true anthracite, free from ash:—

Carbon.		Hydrogen.		Oxygen and Nitrogen.
93 to 95	...	2 to 4	...	3.0

The proportion of nitrogen varies from 0.55 to 2.85 per cent., and that of sulphur from 0.63 to 1 per cent.; ratio, 1:1 to 1:0.5.

Anthracite burns almost without flame, and the carbonaceous residue remaining after distillation shows no signs of caking. The anthracite of Pennsylvania is employed on a large scale in the manufacture of pig-iron. In the United Kingdom this is not the case, as our anthracites will not stand a high temperature without disintegration.

It must be borne in mind that "coal" is a popular rather than a scientific name, as it is frequently applied, not only to beds of fossilised vegetation, but to all mineral substances capable of being used as fuel. According to Frémy,* true coal may be distinguished from lignites by its insolubility in hypochlorites, and its very imperfect solubility in nitric acid.

Coals having widely different properties may be proved by analysis to contain exactly the same amounts of carbon, hydrogen, and oxygen, so that in the respective cases the grouping of these elements must vary greatly. Coals, in fact, may be isomeric.

It is found that the calorific power of true coal and lignites increases with the proportion of coke left by distillation, and the student will do well to bear in mind that the calorific value of a coal may be better estimated by weighing the coke left after strongly heating the coal in a covered crucible than by calculations based on a chemical analysis of the sample. The class to which the coal belongs may also be best determined by this method of distillation in a closed vessel, which enables the relative amounts of water, bituminous matter, and coke to be ascertained. The method of coking in a covered crucible also gives valuable information as to the nature of the coke.

6. **Liquid Fuels.**—Under the general term of *petroleum* is included a series of natural hydrocarbons. These usually occur in nature impregnating clay, marl, sand, and schist, sometimes sufficiently to render the rock combustible. The high percentage of ash in such fuels prevents them from being used direct, and, as a rule, renders it necessary to subject them to distillation, which yields tar products, oils, and gases. The so-called "Boghead mineral," a bituminous schist of the Scotch coal measures, yields—

Ash.		Fixed Carbon.		Combustible Gases.
19.60	...	10.13	...	70.10

Cannel coal is a fuel of a similar character, but with a low percentage of ash. It burns with a long smoky flame, and has the following percentage composition:—

Carbon.		Oxygen.		Hydrogen.		Ash.
85.0	...	8.0	...	5.0	...	2.0

* *Comptes Rendus*, vol. lii. (1861), p. 114.

It yields 42 per cent. of volatile matter. The mineral *jet* is a bituminous lignite. When the bituminous constituents of these rocks occur in sufficient quantity, naphtha and petroleum springs, or deposits of solid asphalt, are formed. At Baku in the Caspian Sea, and in Pennsylvania, mineral oils are obtained in enormous quantities by means of deep bore-holes. The oil regions of Pennsylvania alone have a productive area of 364 square miles, and the total output from 1859 to 1884 was 260,990,035 barrels, each of 42 gallons. In 1893, the United States exported 10,660,000 gallons in a single month.

Petroleum contains a very high proportion of hydrogen, which in the case of the solid bituminous materials may reach 15 per cent. On distillation, from crude petroleum a product is obtained containing 79.82 to 88.5 per cent. of carbon and 11.5 to 20.18 per cent. of hydrogen. The boiling-point of petroleum varies from 110° to 280° , and the calorific power of the crude oil is 10,000 *calories*, a calorific power which is greater than that of refined oil.

The oil is employed in practice by burning it in a trough, by effecting its combustion in a spray or finely divided form by injecting it with a jet of steam or air, or by converting it into gas before combustion.*

7. **Natural Gas.**—In the oil regions of Pennsylvania and of the adjoining States, natural gas issues from the strata at a depth of 500 to 2000 feet below the surface; and when bore-holes are sunk to the accumulated gas, it rises under a pressure of some 200 lbs. per square inch. When first reached, the gas is sometimes evolved at the enormous pressure of 1000 lbs. per square inch. Compared with air the gas has a density of 0.45 to 0.55, and varies in volumetric composition within the following limits:—

CH ₄	H.	N.	C ₂ H ₆	C ₃ H ₈	CO ₂	CO.
60 to 80 ...	5 to 20 ...	1 to 12 ...	1 to 8 ...	0 to 2 ...	0.3 to 2 ...	trace

It has a calorific power of 14,000 to 15,600 *calories*, and a calorific intensity of 2745° to 2765° . Natural gas has long been used in Pennsylvania to a limited extent for heating purposes. Since 1883, however, it has attained a remarkably rapid development for industrial purposes, and is now largely used in Pittsburgh in the blast furnace, and for other metallurgical purposes.

The territory containing the source of natural gas includes a section of country extending from Western New York, through Pennsylvania, into West Virginia and Ohio, and to Canada.

* On petroleum, consult Crew, *Practical Treatise on Petroleum*, Philadelphia, 1887.

In 1884 as much as £292,000 worth of coal was supplanted by natural gas, about two-thirds of this amount representing the consumption of the Pittsburgh district. The freedom of the gas from sulphur has been an important element in its metallurgical value.*

II. PREPARED FUELS.

1. **Compressed Fuels.**—Numerous attempts have been made to prepare a good fuel by mixing some binding material with small coal in proportions sufficient to enable the particles to cohere so as to be pressed into a block or *briquette*. Potato-meal, soluble glass, asphalt, and turpentine have been used as binding materials, but abandoned, whilst coal-tar, pitch, and even treacle have been successfully used for the purpose.†

2. **Dried Fuels.**—The advantages derived from the expulsion of the water and a certain proportion of the more volatile constituents of wood, peat, and lignite have already been pointed out.

3. **Carbonised Fuels.**—On heating fuels without access of air, their constituents re-arrange themselves in the form of solid, liquid, and gaseous compounds. For metallurgical purposes, the object of this operation is often only to obtain the solid constituent, charcoal or coke, which consists of carbon with subordinate amounts of hydrogen, oxygen, and ash-giving constituents, and which has a high calorific intensity. At the same time, the by-products obtained during the carbonisation are frequently utilised. The carbonised fuels to be considered are—(a) charcoal and (b) coke.

(a) **Charcoal.**—This name is given to the carbonised residue remaining after the dry distillation of wood. When wood is heated to 200° without access of air, it remains unaltered; at 220° it becomes brown; and at 270° to 300° it suffers decomposition, torrefied wood (*Rothholz*) being formed. At 350° it is resolved into a fixed residue, or charcoal, and volatile products. Good charcoal prepared at a temperature of 350° to 400° retains the structure of the wood from which it was derived, the volume being less. It is black, porous, and burns without smoke, and, in separate pieces, without flame. The specific gravity of porous charcoal varies from 0.28 to 0.54 according to the nature of the original wood, and the temperature at which it was made.

* On natural gas, consult Phillips, *Rep. Second Geol. Surv. of Pennsylvania*; Carnegie, *Journ. Iron and Steel Inst.*, 1885, p. 168; Ashburner, *Trans. Amer. Inst. Min. E.*, vol. xiv. (1886), p. 428.

† Compare Freissig, *Die Presskohlenindustrie*, Freiberg, 1838.

Charcoal prepared at 350° is considerably lighter than that prepared at the melting-point of platinum. Hard woods give a dense and heavy charcoal, whilst soft woods give soft and friable charcoal. The chemical composition also varies considerably, the percentage composition of charcoal prepared at 340° (I.), and at the melting-point of platinum (II.), being as follows:—

Carbon.		Hydrogen.		Oxygen and Nitrogen.	
I.	75.20	...	4.41	...	19.96
II.	96.52	...	0.62	...	0.94

The ash of the first charcoal was 0.48, and of the second 1.94 per cent. On an average, dry charcoal contains 90 per cent. of carbon, 3 per cent. of hydrogen, and 7 per cent. of oxygen and nitrogen.

The charcoal used in metallurgical operations is prepared by various methods, which may be divided into two groups—viz., methods of coking (1) in the open air and (2) in closed chambers. For charcoal burning in the open air, a suitable site is necessary. This should be dry, and sheltered from any prevailing wind. Water should be at hand for quenching the charcoal when made. The wood employed must be mature, cut while free from sap, barked, and air dried for some months.*

When the charring is effected in circular piles, or *meilers*, the bed is made to slope from the circumference to the centre at an inclination of 1 in 15. Three stakes, 10 to 15 feet high, are driven in near the centre, so as to form a central triangular chimney. Around this, the timber, cut into suitable lengths, is stacked horizontally and radially. The mass is then covered with a mixture of fine charcoal and clay, and then with sods with the grassy side inwards. To keep this covering up, wedges are driven in, and props put in so as to form hoops around the lower part of the pile. Brushwood is then thrown down the chimney, and ignited, vents being made near the top of the pile. This causes a cone, with the apex downwards, of the pile to be charred, and, by opening vents lower down, the angle of the cone is enlarged. This process is continued until the base is reached. When the smoke issuing from the pile is seen, by its blue colour, to be free from aqueous vapour, the charring is complete. The charcoal is then drawn from the bottom of the pile and in small quantities quenched with water or dust. Small piles are carbonised in six to

* On charcoal burning, consult G. Svedelius' *Handbook for Charcoal Burners*, translated from the Swedish by R. B. Anderson and W. J. L. Nicodemus (New York, 1875).

fourteen days; but if the diameter be more than 30 feet, the process occupies a month.

Logs as much as 24 feet in length may be charred in rectangular piles. They are laid together in the form of a wedge, of which the breadth is limited by the length of the logs. The heap is 20 to 30 feet long, and 7 to 9 feet high at the upper end, and only 3 feet high at the lower end. It is surrounded on all sides with a layer of sods and charcoal dust, and by a wooden covering supported by vertical stakes. On the top is placed a roof of twigs, leaves, and charcoal dust. At the lower end, a horizontal chimney is left. Vents are opened at the opposite end so as to give planes of charring. Rectangular piles are used in Sweden and in Austria. In China the carbonisation is effected in pits provided with a chimney communicating with the bottom.

Experiments, on a large scale, on the amount of charcoal yielded gave the following results:—In France, with circular piles of 2120 to 3180 cubic feet, the yield by weight was 17 to 21.3 per cent.; in Belgium, on charring wood fifteen to twenty years old, half hard, half soft, the yield at the ordinary rate was 15 to 17 per cent., but when charred more slowly, 20 to 22 per cent.; in Sweden, from pine wood, the yield was 20 to 28 per cent. By volume, the yield of charcoal varies from 50 to 75 per cent.

By using closed ovens or kilns, the yield of charcoal may be somewhat increased, but as about 5 per cent. is required for heating the oven or retort, the advantages presented are very slight. Peat may be charred, like wood, in heaps or in kilns. Peat-charcoal, however, on account of its lightness, friability, and its high percentage of ash, is not adapted for metallurgical purposes, and its application has not advanced beyond the experimental stage.

(b) **Coke.**—Coke is the carbonaceous residue left on the dry distillation of coal. Good coke should possess sufficient strength to withstand the pressure in a blast furnace without crushing. For this reason, only those coals which give on dry distillation a coherent residue can advantageously be used. The coals of the second, third, and fourth groups of Gruner's classification are suitable for coking. A high percentage of ash has a detrimental influence on the coke produced, and must therefore be removed by subjecting the coal to a preliminary washing.

Coke varies considerably in its external characters. It may be porous and light, or compact and heavy; black and dull, or light-grey and bright, with a semi-metallic lustre. The porosity of coke induces a tendency to absorb gas. Belgian coke for locomotives contains—

Carbon.		Hydrogen.		Oxygen.
97.33	...	0.35 to 0.50	...	2.18 to 2.32

Like charcoal, coke is hygroscopic, absorbing 1 to 2.5 per cent. of water from air at the ordinary temperature. When dipped in water, coke will absorb 20 to 50 per cent. The calorific power of coke, free from ash, is 8000, or almost equal to that of pure carbon.

The earliest method of preparing coke was by carbonising coal in the open air in heaps, without any external covering. A more economical method is by carbonising the coal in mounds, piled round a central octagonal chimney. The mound is ignited at the top, and the operation proceeds exactly as in charcoal burning. The mounds are usually 12 to 21 feet in diameter, and 9 to 15 feet high. The yield after five days' coking is 65 per cent. of the theoretical quantity.

In Upper Silesia, rectangular kilns have been used for coking for many years. They are cheap, easy to work, and give a large output, but, like the mounds, they do not yield a uniformly coked product. They are chiefly used for coking coal slack. These kilns, or Schaumburg coke-ovens, Fig. 46, have two fixed parallel

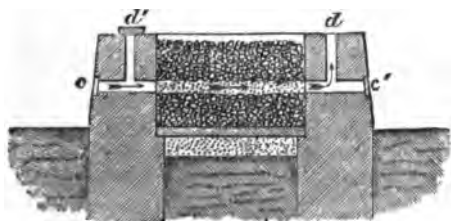


FIG. 46.

walls 18 yards long and 5 feet high. The walls are 8 feet apart, and are provided with a series of square openings 2 feet apart and 1 foot above the sole, the apertures, *c*, in one wall being opposite those in the other. From each aperture ascends a vertical flue, *d*, which may be closed with a tile. In order to charge the kiln one of the open ends is bricked up, and moistened coal slack is stamped in up to the level of the apertures. From the apertures in one wall wood stakes are placed across, the ends passing into the corresponding apertures on the opposite side, and the whole kiln is filled with moistened slack, and covered with loam. On withdrawing the stakes, the passages formed communicate with the horizontal apertures and with the vertical flues in the side

walls. The process consists merely in regulating the air current in the flues, and is complete in about six days. The flues are then closed, and the coke, after cooling for two days, is withdrawn at the open end.

These wasteful methods of coking are now generally superseded by coking in ovens of brick or stone, in which carbonisation is effected mainly by the heat resulting from the combustion of the volatile products evolved during the process, the aim of the coke-burner being to bring air into contact with these gases, but to prevent its contact with the coke formed.

The coke-ovens that have been introduced to obviate the loss of heat occurring in heaps and kilns are of very various types. The simplest form resembles a beehive or a baker's oven. This is a sort of covered-in mound or meiler. It is lined with fire-bricks, and air is admitted through a doorway closed with loosely piled up fire-bricks. There is thus, as in the cases of the mound and kiln, partial combustion in the coking space itself, and so some coke is burnt. The cavity of the oven is 6 to 12 feet in diameter, and $4\frac{1}{2}$ to 9 feet in height. The doorway is about $2\frac{1}{2}$ feet square, and the coke is drawn through it and quenched in the open air. In some cases the coke is cooled in the ovens before it is drawn by watering it by means of a hose. This quenching, by double decomposition, removes some of the sulphur from the coke in the form of sulphuretted hydrogen. Sometimes the ovens have the form of a rectangular chamber 10 feet deep, 12 feet wide, and 10 feet high. The working of the ovens is very simple. On the base, heated from the last charge, or on a layer of slack, the coal ($1\frac{1}{2}$ to $4\frac{1}{2}$ tons) is charged in. The door is then closed, and carbonisation commenced. If the oven was cold, before shutting the door, fire is introduced, and the lower holes in the doorway are left open. The coking proceeds from the top downwards, the draught-holes being successively stopped as the level of the carbonisation sinks. The coking lasts twenty-four to forty-eight hours.

In the improved forms of coke-ovens, air is not admitted into the coking space, but into side flues, so as to mix with the gaseous products passing through openings in the oven walls into the side flues. In this way, use is made of the heat afforded by the ignited gases which are, in the older forms of oven, allowed to pass directly into the chimney or into the open air; there is complete combustion of all the gaseous products, and the ovens are heated without any coke being actually burnt.

All ovens for coking without access of air have a prismatic form, with a quadrilateral section. They may be classed, accord-

ing to the position of the principal axis, into three types—(1) those with a horizontal axis, (2) those with a vertical axis, and (3) those with an inclined axis.

Numerous varieties of ovens with horizontal axes have been introduced, and worked with more or less success. In all these ovens, the object sought is to utilise the gases to the highest possible degree by effecting the coking by their combustion. At first, this led to the adoption of complicated constructions, which have recently been greatly simplified, and the main differences in the system of heating and in the arrangement of flues depend on whether the gases from one coking chamber play on its own walls and floor, or whether the gases from two adjacent ovens are united for heating both chambers, the object being to mix the products of distillation and combustion from coal which has been newly introduced with those from coal which has been longer in the oven.

Of ovens with horizontal axes, the Coppée coke-oven is that most generally in use. It is designed for coking finely divided coal. The Coppée ovens are usually built in series of thirty or forty, and are worked in pairs. The ovens, which are 30 feet long, 18 inches wide, and 4 feet high, have each twenty-eight vertical flues leading from the top through the partition-wall common to two ovens, to the horizontal flues that pass underneath the chambers in the direction of their length. In these horizontal flues, the gases from a freshly charged oven mix with those from one in which the coking is nearly complete, and combustion is effected by air admitted through three small openings. At each end of an oven are two metal doors. The coke is removed from the oven by means of a ram propelled by a cogged driving-wheel worked by a small portable engine. When the coking is complete, the engine and ram are placed opposite the end of the oven, and the coke is pushed out, the operation lasting about two minutes. A jet of water is then applied to the coke. At the same time the lower doors of the oven are closed, and coal is fed in through three openings in the roof, the openings being then covered by sliding doors. The coal is then levelled by means of rakes, and the upper doors are then closed. The whole operation, from the opening to the closing of the doors, lasts only eight minutes. At Dowlais there are thirty of these ovens, numbered consecutively; those with odd numbers are drawn in the morning, and the even twelve hours later, the coking occupying twenty-four hours.

Only one oven, with a vertical axis, has been successfully adopted. This was invented in 1856 by the brothers Appolt,*

* *Annales des Mines*, 5th Series, vol. xiii. (1858), p. 417.

and is now largely used on the Continent. It consists of twelve or more vertical coking chambers of brickwork, arranged in rows, the series being surrounded by walls of brickwork. The ovens are rectangular in plan; they are tapered, measuring, at Saarbrücken, 4 feet 1 inch by 1 foot 7 inches at the lower, and 3 feet 8 inches by 1 foot 2 inches at the upper end, and 16 feet in height. Each oven is surrounded by an air space 10 inches in width, and is provided above with a lid, and below with a door opening downwards into a vault where the coke may be received in an iron waggon. As the charging is also effected by waggons on the top of the furnace, the working is extremely simple. The brickwork of the ovens is separated by air spaces which communicate with one another, and with the interior of the ovens themselves. The products of combustion are carried off to the chimney by means of flues, which have fire-brick dampers for regulating the draught, and in which there are openings to allow of their being cleaned out. The gases from the coal pass into the air spaces surrounding the retort, where they mix with air introduced through flues in the wide sides of the ovens. As in all coke-ovens, the process is conducted by first heating the ovens to redness. They are then filled, and the process may be carried on uninterruptedly. The charge in each chamber is 1 ton 4 cwt. to 1 ton 8 cwt., so that the whole oven cokes about 17 tons of coal in twenty-four hours. The Appolt coke-oven presents the advantage of a very great heating surface in proportion to its capacity, which is easily explained by the fact that each chamber is completely surrounded, with the exception of the two end planes, by fire. Thus, much less heat is lost by cooling from without. Dürre estimates the internal area of the walls at 50 to 58 square feet per cubic yard of capacity, and Kerpely states that the heating surface is more than 1 square foot per 20.5 lbs. of charge. In either case the ratio is double that in the case of horizontal coke-ovens. The average yield of coke is 70 to 80 per cent. with caking coal, and very good results have been obtained with a mixture of caking and non-caking coals. The vertical position of the compartments presents the advantages of occupying less space than other ovens; the coke in dropping down exerts no injurious amount of wear on the sides, and the pressure of the column of coal produces a coke of greater density than that obtained in other ovens. On the other hand, the Appolt coke-oven has the disadvantage of high initial cost, which is double that of any horizontal coke-oven. The cost of an Appolt coke-oven with eighteen chambers is £1500 to £2000. Repairs, too, are effected with much difficulty.

Coke-ovens with inclined axes are used to some extent in the Saarbrücken district. The complicated character of their construction has, however, prevented their general adoption.

Many attempts have recently been made to collect the by-products—ammoniacal liquors and tar—produced during the carbonisation of coal. Henry Simon* calculates that in the British ironworks alone, which produce annually some seven million tons of coke, by the collection of by-products an annual saving of £1,350,000 might be effected. Of the methods in practical operation for collecting the by-products from coke-ovens, that of Simon-Carvès has been most largely adopted. The construction of this coke-oven is somewhat similar to that of the Coppée. There are charging holes, *a, a', a''*, in the top of the oven (Fig. 47). The gases are drawn off through a pipe, *b, b', b''*, which is provided with a regulating valve. From here the gases pass into a system of pipes common to 30–50 ovens, and kept cool by jets of water, so that the tar and ammoniacal liquors are condensed. The lower open ends of the pipes dip into a collector for the products of condensation similar to that employed in many gas-works. The gases from the condenser are then passed through scrubbers filled with moistened coke, where the last traces of ammonia are removed. The uncondensed gases pass onwards to the oven for heating purposes, entering through a horizontal aperture, *c, c'*, in the basal flue of the oven above a grate, *d*, that is filled with ignited coke-dust, whilst the air for combustion enters from below through the grate. Under the base of the oven the burning gases pass to and fro once, then rise between two adjacent ovens to the uppermost of the side flues, *e, e', e''*, and pass gradually downwards to a large flue, *f*, which conveys them to the chimney or under steam boilers. The ovens are 2 to 2½ feet broad and 5½ to 6½ feet high. A greater breadth has not been found to answer. The duration of coking with the smaller oven is from sixty to seventy-two hours. The yield is about 75 per cent. The coke produced possesses sufficient resistance to render it suitable for blast-furnace use.

At the Besaèges Ironworks, in France, the amount of coke produced from ninety-six ovens of this type was 33,092 tons, together with 1099 tons of tar and 4399 tons of ammoniacal liquor. The consumption of coke-dust on the grate did not exceed 35 lbs. per ton of coke produced.

In the recent Carvès oven, the fireplace and grate are dispensed with, and the oven is fired exclusively by the gases escaping con-

* *Journ. Iron and Steel Inst.*, 1880, p. 137.

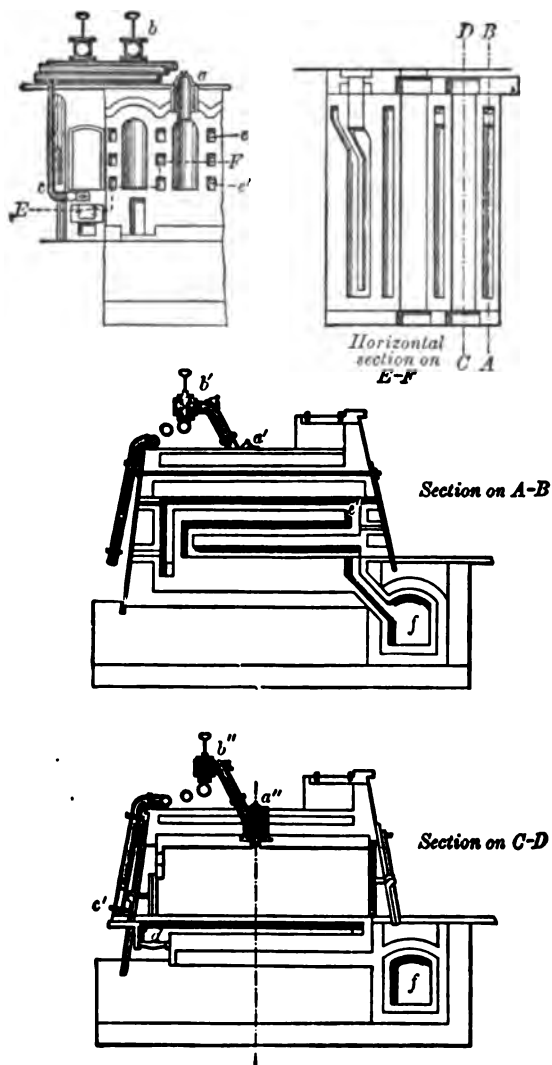


FIG. 47.

densation, these entering the lower flue at the place where the hearth used to be, whilst air is forced in through an annular pipe. In the Simon-Carvès oven* the air introduced receives a previous heating to some 500° or 600° by its being brought into contact with the hot flues conveying away the spent fire-gases from the ovens. The two lower flues are thrown into one, and, at the part of the bottom flue where the greatest heat is sustained, the walls are lined with the best silica bricks. The heated air admitted into the bottom flue is purposely insufficient for complete combustion of the gas introduced there, the further supply of hot air being admitted into the side flues of the oven. The arrangement for thus admitting the air is completely controlled by dampers. At the Bear Park Colliery, Durham, fifty of these ovens have been erected. Each is charged with $4\frac{1}{2}$ tons of coal, the time for coking being a little over forty-eight hours. At Messrs. Pease's collieries, near Crook, Durham, there are twenty-five of these ovens, each 23 feet long, 6 feet 6 inches high, and $19\frac{1}{2}$ inches wide, with side and bottom flues, the capacity being $4\frac{1}{2}$ tons of coal. The average cost of an oven of this description, if a hundred were erected, is calculated to be £180.

The Pernolet coke-oven (Fig. 48) differs but little from the ordinary beehive, but it has a fireplace and grate, and the gas is carried into the upper collecting tube *a*, and returned to the bottom flue, *b*, where it is fired with solid fuel.

At the Almond Ironworks, Falkirk, Mr. H. Aitken† adapted means for the recovery of by-products to the beehive oven. The Aitken coke-oven, as shown in Fig. 49, is a beehive oven fitted with two pipes, *a*, *a'*, for conveying the blast and gas from the condensers through small openings in the roof distributed equally round the circumference, whilst channels, *b*, *b'*, *b''*, in the floor of the oven conduct the collected by-products to an external pipe, *c*, which leads them to the condensers. The main body of the oven measures 5 feet from the opening in the roof for filling in coal to the floor, and has a diameter of 9 feet.

The Jameson coke-oven‡ is another improvement on the beehive oven. It is shown in cross-section and in sectional plan in Fig. 50. In the bottom of the ordinary beehive oven, *a*, channels are formed, covered with perforated tiles, *b*, *b'*, *b''*, connected out-

* *Journ. Iron and Steel Inst.*, 1883, p. 494; 1885, p. 108.

† *Trans. N. Eng. Inst. M.E.*, vol. xxix. (1879).

‡ *Journ. Soc. Chem. Ind.*, vol. ii. (1883), p. 114; *Journ. Iron and Steel Inst.*, 1883, p. 504.

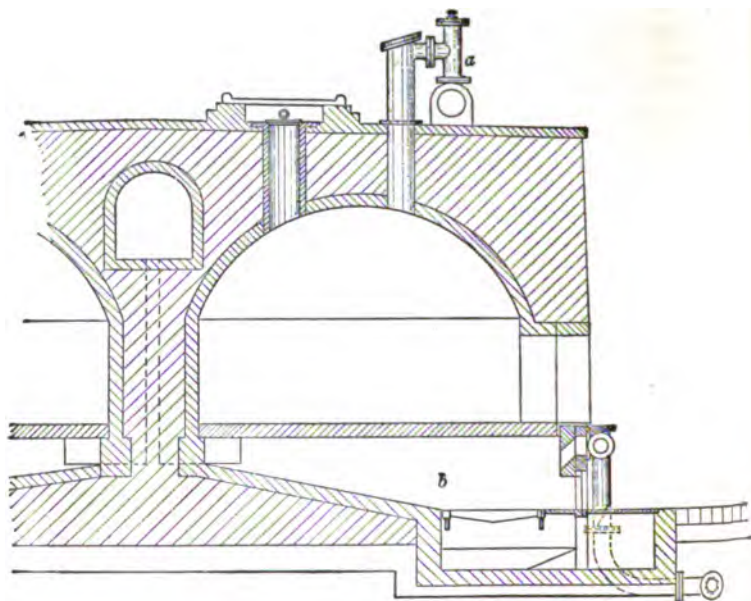


FIG. 48.

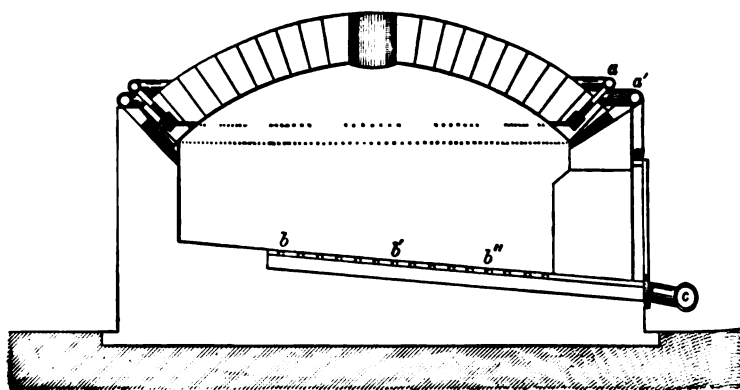


FIG. 49.

side the oven with pipes leading to apparatus, c, c' , for producing a slight suction and for discharging the by-products when required. The cost of applying this process is small, and the results of a series of trials show that the average yield of coke is 65.49 per cent., the average yield of ammonium sulphate and of oil being 4.6 lbs. and 6.1 lbs. per ton respectively.

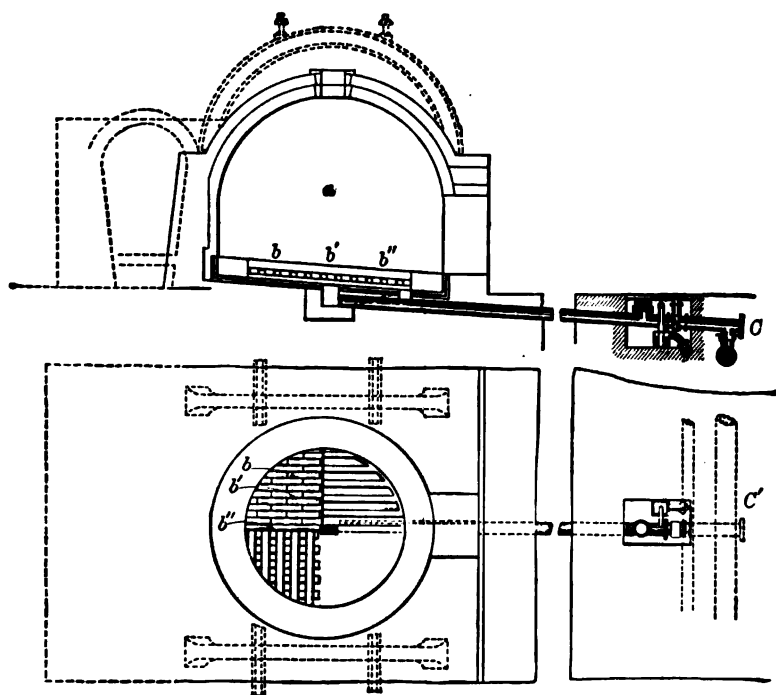


FIG. 50.

The Lürmann coke-oven (Fig. 51) works continuously, and yields a good compact coke. It consists of a large chamber, a , which may be either a huge tunnel or arched as shown in the figure. Opening into this are a number of coking chambers, b, b' , into which fine coal is fed continuously by a piston-feed, worked by a crank from hoppers. The gaseous products pass into a , and, if required to be collected, they are drawn off at an aperture at the top, and thence conducted into the spaces, c, c' , under the

retorts b, b' , where they are burnt by means of air admitted for the purpose. The coke as it falls from the ends of b, b' , is received in a , and is removed at intervals. A great advantage presented by this coke-oven is that it does not need special fire-bricks.

4. **Gaseous Fuel.**—The use of gaseous fuel in metallurgical operations has effected a great saving in coal. Besides this advan-

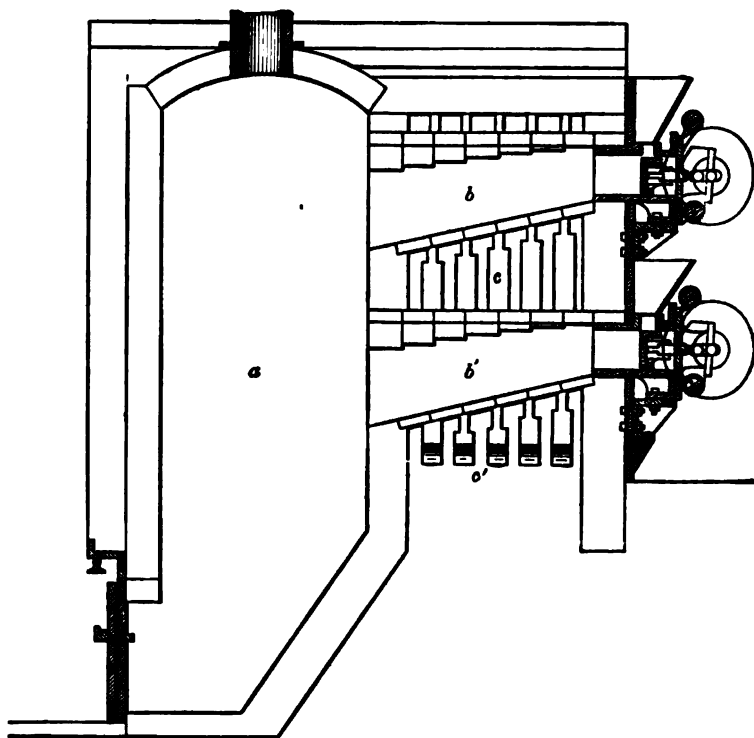


FIG. 51.

tage, there are two circumstances that must lead to its more general adoption ; these are the possibility of employing inferior fuels and waste products, and the high temperatures attainable by the use of such fuel. The method of gas-firing is, however, still far short of a universal adoption, but it may be predicted that, as the sub-

ject becomes more widely understood, the examples of any other method of treating fuel will become rare.

The use of gas as fuel is based on the principle that at one place all the fuel is converted into combustible gas, which is consumed by admixture with the necessary amount of air at another. These gases are produced by burning the fuel in a long column, whereby most of the carbon is burnt to carbonic oxide, whilst the hydrogen either remains free or is converted into carburetted hydrogen. Directly above the grate carbonic anhydride is formed, but this is converted into carbonic oxide on passing through the column of heated fuel above it. The reaction is shown by the following equation:— $\text{CO}_2 + \text{C} = 2\text{CO}$. As a rule, the finer the fuel, that is, the more compactly it lies, the lower is the column required for the reduction of the carbonic anhydride. Besides the products of combustion mentioned above, distillation products are formed in the upper layers of the fuel and mix with the combustible gases. Amongst these, heavy carburetted hydrogen (C_2H_6) is that which principally increases the value of the gas as fuel, and the drier the fuel used the more of this gas is produced.

The conversion of fuel into combustible gas is effected in special apparatus, termed *producers*, from which it is conducted to the furnace, and burnt. For the formation of producer-gases a certain temperature is required, which should not be exceeded. This temperature is dependent on the amount of air introduced. If this is large, complete combustion is effected, and the desired object is only imperfectly attained. If, however, it is too small, the heat is not sufficient for the formation of carbonic oxide, and the evolution of gas ceases. The exact amount of air that should be introduced into a gas-producer can only be determined by experiment.

The composition of producer-gases is, by weight, as follows:—

Fuel Used.	Nitrogen.	Carbonic Oxide.	Carbonic Anhydride.	Hydrogen.
Wood . . .	53.2 to 55.5	21.2 to 34.5	11.6 to 22.0	0.7 to 1.3
Charcoal . .	64.9	34.1	0.8	0.2
Peat . . .	63.1	22.4	14.0	0.5
Coke . . .	64.8	33.8	1.3	0.1

The gas-producer first assumed importance in 1856, on the introduction of the Siemens regenerative system. In 1861 the well-known Siemens gas-producer was patented. It consists of a chamber lined with fire-brick, with one side sloping at

an angle of 45° to 60° , with the grate at the bottom. The grate thus resembles the step-grate largely used on the Continent. The fuel is charged in at the top of the incline, and falls in a thick bed upon the grate, where air is admitted. Passing from the top of a brick shaft or up-take, 8 to 10 feet high, placed above the producer at the back, there is a cooling tube, having not less than 60 square feet of surface per producer. Its object is to cool the gases issuing from the producer, thus giving them increased density, causing an onward movement towards the furnace, and rendering it unnecessary to place the producer at a much lower level than that of the furnace. This cooling, however, results in a condensation of tar, and, to overcome this annoyance, modifications have been adopted in the producer and its working. In the new type of Siemens producer the volatile products of distillation are obliged to descend through highly heated fuel, thus causing the tar to undergo decomposition.

The principal forms of gas-producers are described by Rowan.* Since the introduction of the regenerative principle, many designs for furnaces have been proposed, without separate gas-producers. One of the most successful of these is the Böstius furnace, largely used for zinc-smelting.

The Wilson gas-producer (Fig. 52), working under a slight pressure, presents the advantage of burning fine slack coal. Fuel is introduced in the chamber *A*, through a hopper, *h*. The ashes are drawn by two small doors, *c*, at the bottom every twenty-four hours, the operation occupying about twenty minutes. During this time the production of gas is stopped. The producer represented in the figure has a diameter of 8 feet, and is constructed to burn 4 cwt. of small coal per hour. Air is injected into the chamber by two steam jets, *b*, each having a diameter of $\frac{1}{4}$ inch.

Analyses of gas from the Wilson producer gave the following results :—

	I.	II.	III.
Carbonic oxide	26.89	23.41	23.60
Marsh-gas	1.45	2.22	3.05
Hydrogen	11.55	13.82	10.55
Nitrogen	56.11	55.86	57.55
Carbonic anhydride	4.00	4.69	5.25
Totals	100.00	100.00	100.00
Percentage of combustible gas . .	39.89	39.45	37.20

* *Mina. Proc. Inst. C.E.*, vol. lxxxiv. (1886), p. 2.

I. is from a producer using Durham coal. II. is an average of six samples of gas taken over a time of one hour from a producer working on fine slack from a Yorkshire colliery. III. is from a producer working with coal of the Jemmapes district, near Mons, Belgium.

In 1814 Aubertot first used the waste gases of blast furnaces for roasting ore, burning lime, and similar purposes, and these

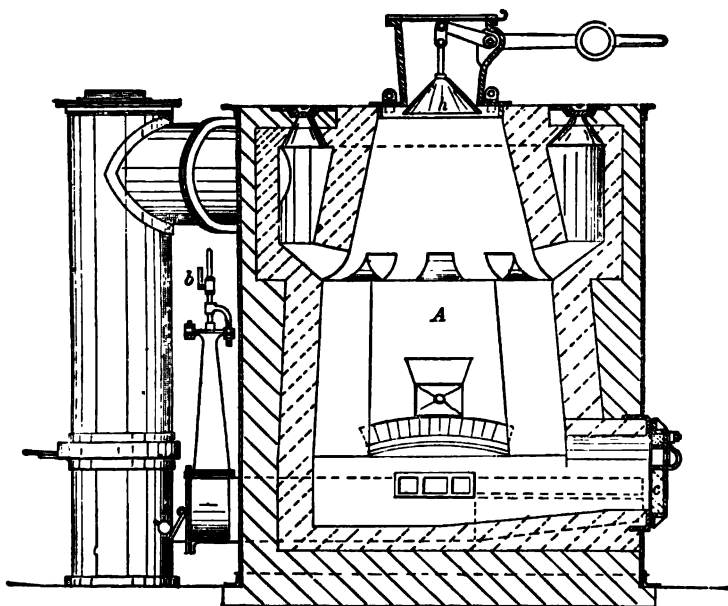


FIG. 52.

gases are now largely used when a very high and uniform temperature is not required. The composition by weight of the waste gases, according to the fuel used in the blast furnace, is as follows :—

	N.	CO.	CO ₂ .	CH ₄ .	H.	C ₂ H ₄ .
Charcoal .	59.7-63.4	20.2-29.6	5.9-19.4	0.3-1.0	0.1-0.4	—
Coke .	64.4	34.6	0.9	—	0.1	—
Coal .	56.3	21.5	15.2	4.2	1.0	1.8

Water-gas.—The gaseous fuel known as water-gas is made in the following manner:—An iron cylinder is lined with fire-brick, and provided with the necessary apparatus for introducing the coke. When this has been lighted, a current of air is forced in until the mass is brought to a high temperature. The blast is then stopped, the charging aperture is closed, and a jet of steam is passed through the incandescent carbon. The steam is decomposed; its oxygen burns the carbon into carbonic oxide, setting free the hydrogen. The resulting mixture is known as water-gas. It consists of one volume of hydrogen and one volume of carbonic oxide, the weights being in the proportion of 2 to 28.

If, by burning one unit of carbon, it were possible to generate one unit of hydrogen, the exchange effected in the water-gas apparatus might be a very profitable one. Such a condition of things is, however, shown by Sir Lowthian Bell* to be directly opposed to the known facts of the case, for 25 per cent. only of the carbon used is burnt to the condition of water-gas, whilst the other 75 per cent. is converted into producer-gas, containing 68 per cent. of inert nitrogen. From 25 parts by weight of carbon there will be generated 62.5 parts of water-gas, containing 4.16 of hydrogen and 58.34 of carbonic oxide. The producer-gas from the remainder (75 parts) of the carbon will weigh 551.19 parts, of which 376.19 will be incombustible nitrogen and 175 carbonic oxide. The following estimate gives the quantity of heat generated by the combustion of the two gases:—

Water-gas . . .	4.16 of H from steam	$\times 29400 = 122304$	
	58.34 of CO	" $\times 2400 = 140016$	262320
			<hr/>
	62.50		
Producer-gas . .	175.00 of CO	$\times 2400$	420000
	376.19 of N		
			<hr/>
	551.19	Calories . .	682320

Had the 100 parts of carbon been burnt direct, the heat generated would have been 800,000 *calories*. The loss is thus 14.71 per cent. Besides this, as coke was used, there is the loss of combustible matter which is incurred at the coke-oven, and the labour in conducting the process of coking.

Sir Lowthian Bell calculates that the relative values of coal, producer-gas, and water-gas are as follow:—

Coal	83.93
Producer-gas	71.14
Water-gas and its producer-gas	78.80

* *Journ. Iron and Steel Inst.*, 1889, No. II. p. 139.

Bibliography.—For fuller information on fuel the student is referred to the following standard treatises :—Percy, *Metallurgy*, vol. i. London, 1861; second edition, 1875; Galloway, *Treatise on Fuel*, London, 1880; Schwackhöfer and Browne, *Fuel and Water*, London, 1885; Phillips and Bauerman, *Elements of Metallurgy*, London, 1887, pp. 16–107; Mills and Rowan, *Fuel and its Applications*, London, 1889; Gruner, *Traité de Métallurgie*, Paris, 1875, vol. i. pp. 36–161; Kerl, *Grundriss der allgemeinen Hüttenkunde*, Leipzig, 1879, pp. 36–198; Muck, *Grundzüge der Steinkohlen-Chemie*, Bonn, 1881; Fischer, *Chemische Technologie der Brennstoffe*, Leipzig, 1887. Schnabel, *Lehrbuch der Allgemeinen Hüttenkunde*, Berlin, 1890.

Much information is also to be found in the *Journal of the Iron and Steel Institute*, 1892. A. Naumann: *Technisch-Thermochemische Berechnungen zur Heizung*, Brunswick, 1893: For the use of students, the series of calculations contained in this work is of much value. The author shows the number of *calories* liberated by the combustion of the chief constituents of coal or producer gas, and gives the specific heats of the combustion products; he next sets a series of questions relating mainly to the combustion of such gas, or of coal, and then gives in each instance the calculations necessary to obtain the answers to the questions set.

CHAPTER VI.

MATERIALS AND PRODUCTS OF METALLURGICAL PROCESSES.

Ores.—This term is applied by the metallurgist only to those minerals from which, on a large scale, metals may be obtained with profit. The ores must be supplied to the works in a suitable condition for smelting, the preliminary washing and dressing operations being carried out at the mine. *Gangue*, vein-stuff, or matrix is the extraneous earthy matter associated with the ore.

Ores contain the metals—(1) in the native or metallic state (examples—gold, silver, copper, mercury); (2) in combination with oxygen as oxides (for example, ferric oxide, tin oxide); (3) as oxides in combination with water (limonite, $\text{Fe}_2\text{H}_2\text{O}_4$); (4) in combination with halogens (silver chloride); (5) in combination with sulphur, arsenic, and antimony (galena, PbS); (6) in combination with acids as salts (anglesite, PbSO_4); ores also occur in nature in a state of mixture; (7) as various combinations of the same metal (for example, azurite, $2\text{CuCO}_3 + \text{Cu}(\text{HO})_2$); (8) as various combinations of more than one metal in one mineral species (for example, pyrargyrite, $3\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$); lastly, (9) as several mineral species occurring together in the ore-deposit, galena and blende, spathic iron ore and iron pyrites.

The value of an ore depends upon the nature of the metal it contains and the difficulty with which its extraction is attended. Thus, iron ores containing less than 30 per cent. of metal are rarely smelted. Ores of iron, lead, or zinc are not considered rich unless they contain 50 per cent. of metal. Copper ores are rich when they contain 25 per cent. of metal, whilst ores yielding a few ounces of gold per ton are extremely valuable.

Fluxes.—In order to separate the extraneous matter usually contained in a furnace charge of ore and reducing agent, certain materials must be added to form slag. These materials are known as fluxes.

In the smelting processes earthy, alkaline, and metallic sub-

stances are used as fluxes. The alkaline fluxes are expensive, and are rarely used except in refining processes. The following are the principal earthy fluxes in use:—

1. Lime, which acts as a powerful base for removing silica. Lime is used in a pure state or as carbonate. As a rule, limestone is used, especially if the furnace is large. Limestone is largely used in iron smelting, as most iron ores contain unsaturated silica. Dolomite, the carbonate of lime and magnesia, is specially useful.

2. Fluorspar (calcium fluoride), which is a useful flux for ores containing silica, barytes, or gypsum. With the two latter it easily fuses. It has also been used for removing phosphorus from iron ores in the blast furnace, but on account of its expense its employment, though advantageous under all conditions, is limited. The greater portion of the fluorspar is found unchanged in the slag; it facilitates the fusion, and increases the fluidity of the mass.

3. Barytes, which acts as a powerful base. It is a good sulphurising agent, for example, in the concentration of nickel speise, the copper present with the speise being removed and a regulus formed.

4. Alumina-bearing rocks, such as clay-slate, are used in smelting ores very rich in lime. As a rule, however, the charge is so mixed that argillaceous and calcareous ores are present in suitable proportions.

5. Siliceous materials, such as quartz, natural silicates, siliceous slags, are used when the ores contain an excess of basic materials that have to be removed.

Metallurgical Agents.—The metallurgical agents chiefly used are—1. Metals, either for decomposing the combinations of other metals, or as a means of concentration. Thus, iron is used for decomposing galena, zinc for desilverising argentiferous lead, and mercury for concentrating gold.

2. Metallic oxides are used for purifying the raw metal in refining processes. Thus, iron ore or hammer-scale is used for refining iron, and as a flux in lead smelting.

3. Slags serve to increase the fluidity of the furnace charge; or mixtures of slags may be used for recovering the metals they contain, and lastly for preventing "scaffolding" or choking of the furnace when pulverised ores are smelted. Their chemical action varies with their composition; basic slags are able to take up a large proportion of silica, while acid slags readily absorb bases. Alkaline slags are rarely used except in crucible processes, as in assaying.

4. Iron pyrites (FeS_2) and magnetic pyrites (Fe_3S_4) exert a reduc-

ing action on oxides by giving up sulphur and forming sulphurous anhydride. Certain sulphides, such as zinc sulphide, infusible alone, may be rendered fusible by the addition of iron pyrites.

In the roasting of ores in furnaces or in piles the following chemicals are used:—(1) Salt for the formation of silver chloride in the treatment of silver ores; (2) Lime for the absorption or separation of the acids formed on roasting copper regulus, &c.; (3) Ferrous sulphate in the treatment of silver ores containing a little iron pyrites.

Selection of Fluxes.—In the choice of fluxes, when the gangue is siliceous, at least two bases must be added in order to form a fusible silicate. When the gangue is argillaceous, a single base is sufficient to form a double silicate. When the gangue is basic, that is, containing lime, magnesia, alumina, or iron, a siliceous flux must be added. Quartz alone is sufficient if the gangue already contains two or more bases, but, if there is but one base, clay or some other silicate must be added with the quartz. Siliceous slags may be advantageously used for the purpose.

Slags.—The silicates formed in metallurgical processes by the combination of silica with the earths and metallic oxides are termed *slags*. As a rule, slags are smelters' refuse. In the refining of metals, however, slags are frequently formed by the oxidation of the metallic impurities. Such slags consist largely of metallic oxides, and are smelted again in order to recover the large proportion of metals they contain. These slags may be distinguished as cinder or scoria. The quantities of these slags obtained are not very great, and they may therefore be more conveniently regarded as ores.

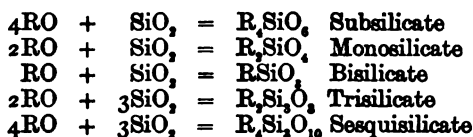
The bases that occur in silicate-slags, mostly combined with the silica, are—lime, alumina, magnesia, rarely ferric and manganic oxides, ferrous oxide, manganous oxide, zinc oxide, more rarely baryta, and alkalis in slags of all blast-furnaces using charcoal as fuel, and, in addition to these, small amounts of the metals that are being smelted are invariably present, partly in chemical combination with the silica, and partly in other combinations mechanically mixed with the slag.

Some oxides and earths, such as zinc oxide and alumina, not only interfere with the fluidity of the slag, but also cause a scum to form which is difficult to separate from the slag. In many slags, calcium fluoride is found. This is frequently the case in the slag from cupola furnaces, as fluorspar is often used as a flux in re-melting pig-iron. The calcium fluoride melts without decomposition, and is merely in a state of mechanical mixture

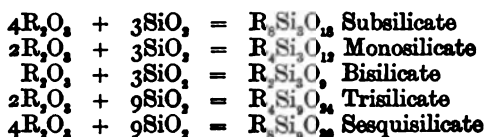
with the slag. This is also the case with the calcium sulphide frequently met with in blast-furnace slags.

The chemical composition of slags is variable. If a slag is distinctly crystallised, it may generally be assumed to have a definite chemical composition, and a formula may be calculated for it. If, however, it is not crystallised, nor even crystalline, it must be regarded either as a mixture of several silicates or as a solution of one silicate in another.

Silica consists of one atom of silicon and two atoms of oxygen, so that the various silicates have the compositions given below. $2RO + SiO_2$ is the monosilicate or neutral silicate of the metallurgist. It contains in acid and base equal amounts of oxygen, whilst the neutral silicate of the chemist, which has the formula $RO + SiO_2$, is termed a bisilicate by the metallurgist, because the acid contains twice as much oxygen as the base. Proceeding from the monosilicate, the following series of formulæ are obtained for silicates:—



For bases having the composition R_2O_3 , the formulæ are—



The quantities of oxygen in the bases bear the following proportions to those in the acids in the various silicates:—

	O in base : O in acid.
Subsilicate	2 : 1
Monosilicate	1 : 1
Bisilicate	1 : 2
Trisilicate	1 : 3
Sesquisilicate	2 : 3

Every sesquisilicate may be resolved into a monosilicate and a bisilicate; thus $R_4Si_3O_{10}$ is equal to $R_2SiO_4 + 2(RSiO_4)$ and $R_4Si_9O_{26}$ is equal to $R_2Si_3O_{12} + 2(R_2Si_3O_9)$. If a silicate contains but one base, it is termed a monobasic or simple silicate, but if two or more bases are present, it is termed a double silicate or a

multibasic silicate, and in the formula the silicates of the various bases are united by a plus sign.

A classification of the silicates as ortho- and meta-silicates, based upon their analogies to phosphates, was suggested by Odling;* but it has not come into use amongst metallurgists.

The fusibility of slags is dependent on the amounts of silica and bases they contain. The subsilicates are very fusible, forming a limpid liquid; they consolidate very rapidly and split up in so doing. They have usually a dark colour and, on account of the large proportion of bases they contain, a high specific gravity. The monosilicates are less fusible, and do not form so limpid a liquid. The bisilicates are less fusible still; they form a viscous mass which may be drawn out into threads. They are usually glassy and consolidate slowly. The trisilicates also flow very slowly, consolidate slowly, and require a very high temperature for their formation.

The most fusible silicates are those of the alkalis, then follow those of lead, iron, manganese, and copper, and finally, the earthy silicates. The simple silicates are always less fusible than the double silicates.

Economic Application of Slags.—The slags obtained in smelting metals other than iron are largely used as fluxes in various metallurgical processes for taking up either the silica or the bases, or, when they are ferruginous, for precipitating purposes. Occasionally the slags are moulded into bricks, and used for walls or other constructions in which no great weight has to be sustained.

The slags obtained in iron smelting are used, if not too glassy, for macadamising roads. For the ballast of railway lines, glassy slags may advantageously be used, as the mass is very permeable and keeps the sleepers dry. In the form of large blocks, they may be used for road making. They may be moulded into bricks, the best results being obtained when the moulded bricks are kept at a white heat for several hours in a tightly closed space, whereby they are devitrified and become considerably harder if they are allowed to cool slowly under a cover of coal dust and ashes. Good bricks may be made of granulated slag mixed with lime, the proportions being usually 10 parts of slag-sand to 1 part of lime. Blast furnace slag, if not too acid, may be burnt in a state of powder with lime, and gives an hydraulic cement almost equal to Portland cement.

The manufacture of slag cement has of recent years acquired

* *Phil. Mag.*, vol. xviii. (1859), p. 368.

so considerable a development that it may safely be said that an advantageous method of utilising blast-furnace slag has at length been found. The following are analyses of slags actually used for this purpose:—

	Middlesbrough.	Bilbao. Spain.	Sanlines. France.	Choindez. Switzerland.	Harzburg. Germany.	Belgium.
Lime	32.75	47.30	47.20	45.11	48.59	44.75
Silica	30.00	32.90	31.65	26.88	30.72	32.51
Alumina	28.00	13.25	17.00	24.12	16.40	13.91
Ferrous oxide	0.75	0.46	0.65	0.44	0.43	0.48
Magnesia	5.25	1.37	1.36	1.09	1.28	2.20
Calcium sulphide	1.90	3.42	—	1.86	2.16	4.90
Manganese oxide	0.60	1.13	0.85	0.50	traces	0.60
Residue	0.75	0.17	1.29	—	0.42	0.65
Totals	100.00	100.00	100.00	100.00	100.00	100.00

The slag is run into water so as to render it easy to obtain slag-sand. This is ground under edge-runners, and the pasty mass is spread on drying plates. The dried slag is then ground under millstones to a fine powder and sifted to exclude coarse particles. Freshly burnt lime is slaked, and then carefully screened, and 25 per cent. of this slaked lime is thoroughly mixed with 75 per cent. of slag-sand. Grosclaude* estimates the entire cost of works and plant for an annual output of 6000 tons at £6000.

The specific gravity of this cement is very low as compared with Portland cement, whilst the time occupied in setting is comparatively long. For purposes of storage it compares well with Portland cement. By exposure to the air it absorbs carbonic anhydride more rapidly than does Portland cement, but it does not deteriorate greatly by long exposure. Owing to the closeness of the particles, this cement appears to be well adapted for works under water, such as docks or breakwaters.

Blast furnace slag is also largely used for the production of slag wool, or silicate cotton, which is obtained by causing steam to impinge on to a jet of molten slag in such a way that the steam jet encounters only a half of the slag jet. Slag wool is extremely light and fire proof. It is a good non-conductor of heat and of sound, and it is so porous that it will absorb large quantities of water. It is used for covering steam and hot-air pipes. In Silesia and other localities, where ironworks and

* *Annales Industrielles*, 1889, p. 90.

collieries are in close proximity, blast-furnace slag is largely used for filling the excavations from which the coal has been removed. Finely pulverised blast-furnace slag has been found in Sweden to be an excellent manure for moorland which is deficient in lime, as well as for clay and sandy soils.

The slag obtained in the basic Bessemer process, on account of its high percentage of phosphorus, forms a valuable manure. Many thousands of tons of slag are annually employed for this purpose, it having been found that the phosphorus it contains is in a form that is very readily assimilated by the soil. The utilisation of basic Bessemer slag is referred to in a subsequent chapter.*

Calculation of Furnace Charges.—In order to obtain the greatest possible yield of metal with the least consumption of fuel, care must be taken to have a proper mixture of ore and flux. Ores reducible with difficulty should be mixed with fluxes that render the charge pasty, so that the slag-forming constituents do not melt before the metals are reduced from their combinations. When raw coal or coke is used as fuel, the quantity and composition of the ash must be taken into consideration, as this always contains silica. With charcoal as fuel, this may be neglected, as the percentage of ash is always low, and the ash itself, which is strongly alkaline, is a useful flux.

As an example of the calculations necessary, a charge of iron ore may be selected which is to be smelted with coke to grey pig iron, and for which the necessary amount of lime as flux is required to be determined. Experience has shown that in coke blast-furnaces, monosilicate slags should be produced, whilst in charcoal furnaces sesquisilicates to bisilicates are found most advantageous. For this example the author is much indebted to Professor C. A. M. Balling, Director of the School of Mines at Příbram in Bohemia, who has permitted him to borrow it from his valuable treatise on metallurgical chemistry.†

Let it be assumed that there are to be smelted four varieties of ore having the following compositions:—

	Fe.	Al ₂ O ₃ .	CaO.	MgO.	SiO ₂ .	S.
A.	54	7	2	—	12	—
B.	47	8	1	1	15	—
C.	38	10	2	1	24	1
D.	40	9	2	1	20	—

In order to simplify the calculations whole numbers are taken,

* Methods of utilising slag are fully described by G. Redgrave, *Journ. Soc. Arts*, vol. xxxviii. (1890), p. 221.

† *Compendium der metallurgischen Chemie*, Bonn, 1882.

and the percentages of water and carbonic anhydride are disregarded. The ore to be used as flux (I.) and the 10 per cent. of ash (II.) in the coke have the following percentage compositions:—

	Fe.		Al ₂ O ₃ .		CaO.		MgO.		SiO ₂ .		S.
I.	25	...	4	...	25	...	4	...	6	...	—
II.	12	...	35	...	1	...	1	...	44	...	0.5

For the production of 100 parts by weight of iron 190 parts by weight of coke are necessary.

In view of the large proportion of silica in the ores C and D, high percentages of these ores are inadmissible in the charge. The ore A, on the other hand, is the best, and must therefore form the greater portion of the charge, which is to be mixed so as to contain on an average 45 per cent. of iron. Taking into account the important constituents of the ores, the following weights would be selected for the charge:—

Ore B.	Ore C.	Ore D.	Flux.	Total.
25	10	15	15	65

It must now be calculated how much iron and slag-giving constituents this mixture contains, in order to determine the quantity of ore A that must be added to give an average of 45 per cent. of iron. In this way, by proportion the following amounts of the various constituents are calculated to be present:—

	Fe.	Al ₂ O ₃ .	CaO.	MgO.	SiO ₂ .	S.
25 parts of B contain .	11.75	2.00	0.25	0.25	3.75	0.10
10 " C " .	3.80	1.00	0.20	0.10	2.40	
15 " D " .	6.00	1.35	0.30	0.15	3.00	
15 " flux " .	3.75	0.60	3.75	0.60	0.90	
65 Totals .	25.30	4.95	4.50	1.10	10.05	0.10

Regarding this ore-mixture as a single ore the percentage composition will be as follows:—

Fe.	Al ₂ O ₃ .	CaO.	MgO.	SiO ₂ .	S.
38.92	7.61	6.92	1.69	15.46	0.15

With this ore, or rather mixture containing 38.92 per cent. of iron, it is required to mix the ore A so as to bring the charge to 45 per cent. of iron. If the ore mixture is represented by x , we have the following equation:—

$$x + A = 100$$

$$38.92 x + 54 A = 100 \times 45$$

On solving this equation, A is found to be 40.5, and $x = 100 - A = 59.5$ parts by weight. The equation thus requires that 40.5 parts of the ore A should be mixed with 59.5 parts of the ore-mixture chosen, and consequently the 65 parts must be reduced by proportion to 59.5, giving the following percentages as the definite composition of the charge:—

Ore A.	Ore B.	Ore C.	Ore D.	Flux.	Total.
40 ...	23 ...	10 ...	13 ...	14 ...	100

In this charge the percentages of the various constituents are found by proportion to be as follows:—

	Fe.	Al ₂ O ₃ .	CaO.	MgO.	SiO ₂ .	S.
In 40 parts of A . . .	21.60	2.80	0.80	—	4.80	
23 " B . . .	10.80	1.84	0.23	0.23	3.45	
10 " C . . .	3.80	1.00	0.20	0.10	2.40	
13 " D . . .	5.20	1.17	0.26	0.13	2.60	
14 " flux . . .	3.50	0.56	3.50	0.56	0.84	
100 Totals . . .	44.90	7.37	4.99	1.02	14.09	0.10

For the production of 100 parts of iron,

$$100 : 45 = x : 100$$

$x = 222.2$ parts of this charge are required, and in this are contained the following weights of iron and slag-giving constituents:—

Fe.	Al ₂ O ₃ .	CaO.	MgO.	SiO ₂ .	S.
99.77 ...	16.40 ...	11.09 ...	2.26 ...	31.30 ...	0.22

For its production, 190 parts of coke are required, the ash of which, according to the analysis, contains:—

Fe.	Al ₂ O ₃ .	CaO.	MgO.	SiO ₂ .	S.
2.28 ...	6.65 ...	0.19 ...	0.19 ...	8.36 ...	0.95

It is therefore necessary to remove as slag: Al₂O₃ 23.05; CaO 11.28; MgO 2.45; SiO₂ 39.66; S 1.17.

For the formula: Al₄Si₂O₁₄ + Ca₂SiO₄ + Mg₂SiO₄, representing a monosilicate, the amount of silica slagged by the bases may be found by proportion with the aid of the atomic weights, thus:—

$$\begin{aligned} 2\text{Al}_2\text{O}_3 : 3\text{SiO}_2 &= 205.6 : 180 = 23.05 : x ; x = 20.18 \\ 2\text{CaO} : \text{SiO}_2 &= 112 : 60 = 11.28 : y ; y = 6.04 \\ 2\text{MgO} : \text{SiO}_2 &= 80 : 60 = 2.45 : z ; z = 1.83 \end{aligned}$$

giving a total $(x + y + z)$ of 28.05 parts by weight of silica, so that $39.66 - 28.05 = 11.61$ parts of silica remain to be converted into slag. According to the same proportion—

$$\text{SiO}_2 : 2\text{CaO} = 60 : 112 = 11.61 : a$$

From which α is found to be 21.7 parts by weight of lime base, which, as calcium carbonate contains but .56 per cent. of CaO, is contained in 38.7 parts of calcium carbonate.

Similarly for removal as calcium sulphide, the sulphur requires, according to the proportion $S : CaO = 32 : 56 = 1.17 : \beta$, $\beta = 2.05$ parts of lime, which amount is contained in 3.65 parts of calcium carbonate. Consequently, altogether there is required $38.7 + 3.65 = 42.35$ parts of calcium carbonate. But as this is added in the form of impure limestone containing only some 95 per cent. of calcium carbonate, the quantity to be added will be 44.58 parts. As this amount, however, is required for 222 parts of charge, 100 parts will require 20.1 parts of limestone as flux. In this example, the small quantity of limestone required is explained by the fact that 14 parts of fluxing ore, containing 25 per cent. of lime, have already been added.

All these tedious calculations may be reduced to a few multiplications and additions by employing the accompanying table that has been computed by Professor Balling :—

TABLE A. For ascertaining the necessary amounts of Bases to convert given amounts of Silica into slag.		TABLE B. For ascertaining the necessary amounts of Silica to convert given amounts of Bases into slag.	
One part by Weight of Silica requires—	Parts by Weight of Bases.	One part by Weight of Base requires—	Parts by Weight of Silica.
For Monosilicates—		For Monosilicates—	
Lime	1.86	Lime	0.535
Magnesia	1.33	Magnesia	0.750
Alumina	1.14	Alumina	0.873
Ferrous oxide	2.40	Ferrous oxide	0.416
Manganous oxide	2.36	Manganous oxide	0.422
For Bisilicates—		For Bisilicates—	
Lime	0.93	Lime	1.070
Magnesia	0.66	Magnesia	1.500
Alumina	0.57	Alumina	1.747
Ferrous oxide	1.20	Ferrous oxide	0.833
Manganous oxide	1.18	Manganous oxide	0.845
For Sesquisilicates—		For Sesquisilicates—	
Lime	1.24	Lime	0.803
Magnesia	0.88	Magnesia	1.125
Alumina	0.76	Alumina	1.310
Ferrous oxide	1.60	Ferrous oxide	0.625
Manganous oxide	1.57	Manganous oxide	0.633

In order to show the simplicity of the use of this table, the same problem may be solved with its aid. For ascertaining the amount of silica converted into slag by the bases in the charge, Table B. is used. In the section for monosilicates, the corresponding figures are found for the bases present, and these figures multiplied together give the following products:—

Al ₂ O ₃	23.05	x	0.873	=	20.12
CaO	11.28	x	0.535	=	6.04
MgO	2.45	x	0.750	=	1.84

Total = 28.00

Thus 28.00 parts of silica (28.05 in the previous calculation) are converted into slag, and of the total amount, 39.66 parts of silica present, there remain $39.66 - 28.00 = 11.66$ parts to be converted into slag by the addition of lime. On referring to Table A., it will be seen that the corresponding amount of lime is 1.86, the product being $11.66 \times 1.86 = 21.69$. Lastly, for the formation

of calcium sulphide, 1 part of sulphur requires $\frac{56}{32} = 1.75$ of lime,

and there is 1.17 part of sulphur to be passed into the slag. This requires $1.17 \times 1.75 = 2.047$ parts of lime. Thus, altogether $21.69 + 2.047 = 23.737$ parts of lime are required. One part of lime is contained in $\frac{100}{56} = 1.785$ of calcium carbonate, the re-

quired addition of limestone as flux is therefore $23.737 \times 1.785 = 42.37$ parts (as compared with 42.35 in the previous solution).

In order to entirely obviate the necessity for any calculation whatever, Professor Balling has devised a method of solving the problem graphically. The method is based on the similarity of triangles. From any point *a* (Fig. 53), two lines are drawn at right angles, and these form two sides of a right-angled triangle. The co-ordinate lines are divided into equal parts. If as many parts of one line are taken as there are equivalents of acid in the slag to be formed, and, similarly, as many parts of the other line as there are equivalents of base, and if the end points of the two sides of the triangle are joined by the hypotenuse, then it is merely necessary to draw from any given point in one side a line parallel to the hypotenuse in order to find on the two sides the equivalent amounts of base and acid in the given silicate.

Fig. 53 is a reduced sketch of the triangles for the monosilicates of the earths that are usually required. For practical purposes, the best unit of length to adopt is the centimetre, so that tenths (millimetres) and half-tenths may be read. As, however, the triangles on this scale would be too large, and as only lower

figures are used, the triangles may be drawn on a reduced scale, for which the following scheme will be found to answer under all conditions :—

The lime monosilicate requires for base $2\text{CaO} = 2 \times 56 = 112$ units of length, and for perpendicular $1\text{SiO}_2 = 60$. The magnesia monosilicate requires for base $2\text{MgO} = 2 \times 40 = 80$, and for perpendicular $1\text{SiO}_2 = 60$. Lastly, the alumina monosilicate requires for base $2\text{Al}_2\text{O}_3 = 2 \times 102.8 = 205.6$, and for perpendicular $3\text{SiO}_2 = 3 \times 60 =$

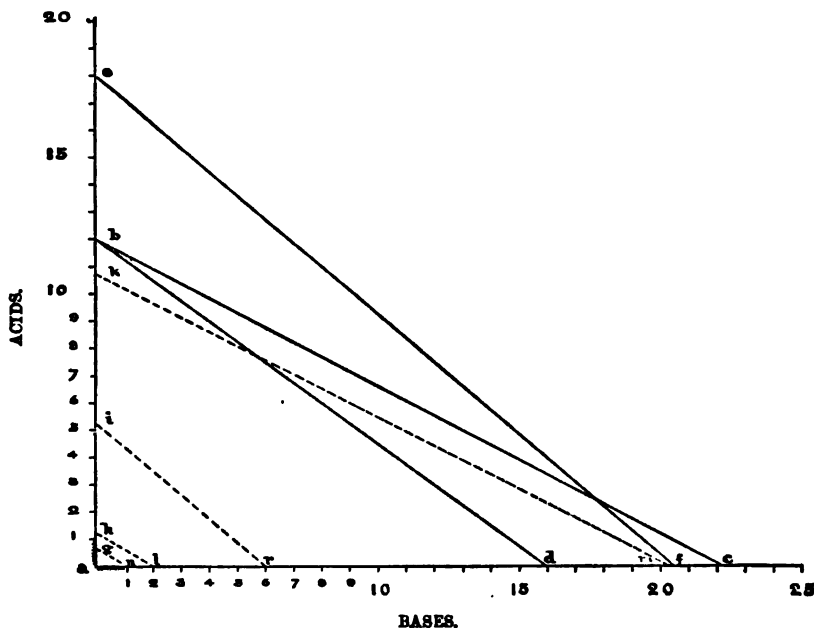


FIG. 53.

180. These lengths are reduced in the triangles for monosilicates of lime and magnesia by one-fifth, and in the triangle for the monosilicate of alumina by one-tenth. Thus the triangle, $a b c$, is that of the lime silicate, $a b$ containing $\frac{60}{5} = 12$ units of length for silica, and $a c \frac{112}{5} = 22.4$ units for lime. Similarly, in the

triangle, $a b d$ representing the magnesia silicate, $a b$ contains 12 units for silica, and $a d \frac{80}{5} = 16$ units for magnesia. Lastly, in the triangle, $a e f$, representing the alumina silicate, $a e$ contains $\frac{180}{10} = 18$ units for silica, and $a f \frac{205.6}{10} = 20.56$ units for alumina.

As an illustration of the application of the graphic method, let it be assumed that in a coke blast-furnace, a charge has to be smelted in which the constituents to be converted into slag average—

CaO.		MgO.		Al ₂ O ₃ .		SiO ₂ .
2	...	1	...	6	...	18

The amount of lime to be added is determined in the following manner:—In order to determine the amount of silica converted into slag by the bases already present, from the point l , representing the units of base (in this case 2 parts), a line is drawn parallel to the hypotenuse $b c$ of the lime triangle. This cuts the perpendicular, representing the silica units, at the point h , and the length $a h$ represents the units of weight of silica which slag off the lime already present in the charge. Similarly, the line $g n$ drawn parallel to $b d$, shows the amount of silica required by one part of magnesia, and the line $i r$, drawn parallel to $e f$, that required by 6 parts of alumina. On measuring these lengths with the dividers on a decimal scale they are found to be: $a h = 1.17$; $a g = 0.75$; $a i = 5.23$, giving a total of 7.15 units as the amount of silica slagged by the bases present in the charge, and there consequently remains $18 - 7.15 = 10.85$ parts of silica to be converted into slag by the addition of lime. If, then, from the point $k = 10.85$ parts of silica, a line is drawn parallel to the hypotenuse of the lime silicate, it cuts the base line at the point m , which represents 20.15 parts of lime, an amount contained in $20.15 \times 1.785 = 35.9$ parts of calcium carbonate.

This method is extremely rapid, and, with careful graduation, gives results of great accuracy. In order to apply the method to bisilicates, the amount of silica must be doubled, or those of the bases must be halved.

A purely mechanical method possesses certain advantages, and Professor Balling's table has been simplified by Mr. H. O. Jenkins, who has devised a special slide rule for the use of the students of the Royal School of Mines, by the aid of which the calculations can be made with great facility. It consists of two equal scales at right angles, one of which (a) is fixed to a small board, whilst

the other (*b*) is fixed at right angles to *a* upon a block (*c*), which is capable of sliding motion in a groove.*

The point A, given by the intersection of the zeros of the two scales, is marked upon the board, and from it a line AB parallel to the groove is drawn. With A as centre, lines AC, AD, AE, are also drawn, making with AB angles whose tangents are equal to the ratios between the weight of silica to weight of base in the respective silicates which it is desirable to produce in order to form

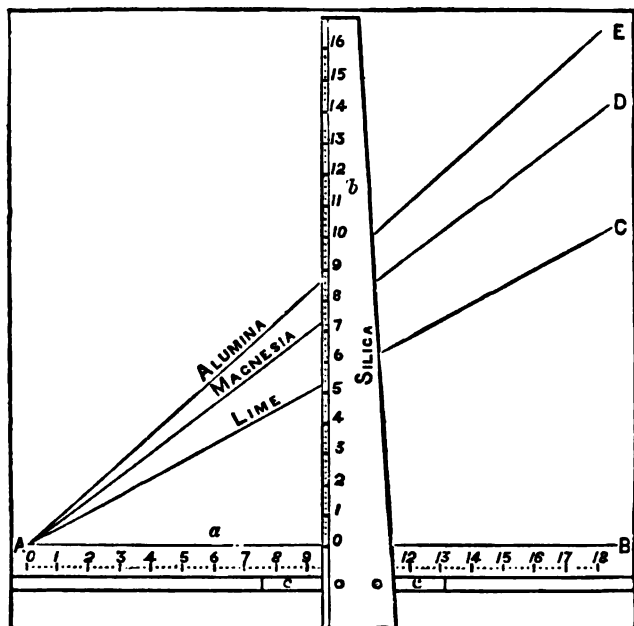


FIG. 53a.

the typical fusible slags ordinarily met with in blast furnace practice. The lines AC, AD, AE, are marked with the names of the bases for which they have been calculated. Thus AC makes an angle of $28^{\circ} 10'$ with AB, this angle having a tangent whose value is 0.5357, which is the ratio of the atomic weight of silica to

* *Journ. Iron and Steel Inst.*, part i. 1891, p. 151.

twice the atomic weight of lime, and corresponds to calcium silicate; this line therefore is marked "Lime."

Similarly the line AD makes an angle of $36^{\circ} 52'$ with AB, the value of whose tangents is 0.75, or the ratio of the atomic weight of SiO_2 to the atomic weight of 2MgO ; hence it is marked "Magnesia."

Also the line AE is at an angle of $41^{\circ} 25'$, and this, having a tangent corresponding to the ratio of the atomic weight of 3SiO_2 to that of $2\text{Al}_2\text{O}_3$, makes the line correspond to the values of the component parts of silica and of alumina in aluminium silicate, and so it is marked "Alumina."

With such a scale it is a very simple matter to at once read off either the excess of silica in any ore, or the amount required to properly flux off the earthy bases present.

As an example, take an ore containing :—

		Silica Required.
FeO	. . . 50	...
MgO	. . . 3	2.25
CaO	. . . 5	2.68
Al_2O_3	. . . 3	2.65
SiO_2	. . . 3	...
CO_2	. . . 36	...

Then setting the movable scale *b* against 3 on the fixed scale *a*, and looking along *b* until the line marked "Magnesia" cuts it, the value 2.25 is found as being the amount of silica required to satisfy the magnesia. In like manner, the amount (2.68) of silica required for the lime is found, and the amount (2.65) for the alumina respectively; adding all these together, the total of 7.58 parts of silica required for every hundred of the ore, is obtained. But there are already three parts present, so every hundred parts of the ore require $7.58 - 3 = 4.58$ parts of silica to flux it. The gangue of the ore is basic to that extent, and the ore itself can be ticketed in the works as :—

C. 607.

Fe. 38.8 per cent.

Basic gangue, needing 4.58 per cent. SiO_2 .

Another parcel of ore might be found to be deficient in bases, and to require, say, bases to neutralise four parts of silica to every hundred parts of ore. If it contained 35 per cent. iron, its label might be—

E. 1000.

Fe. 35 per cent.

Acid gangue, yielding 4 per cent. SiO_2 .

If there is any considerable proportion of ash from the coke, as is often the case, it can be entered as acid or basic, just as in the case of an ore, thus :—

Acid, yielding 2 per cent. silica,

or ;—

Basic, requiring 1 per cent. silica,

and the amount of silica for each part of iron present added (or deducted, as the case may be) to each ore in proportion to the number of parts of iron contained in it.

Any small quantity of sulphur can be considered to be one half its own amount of silica, or a special vertical scale employed, the length of its divisions being as 28 : 60.

If, as is usual, several kinds of ores are to be smelted together, they should, for convenience, be subjected to a preliminary mixing, so as to reduce them to three only. Of these, one should have *less*, and another *more* iron than is required in the final charge, and one should be acid and another basic after the correction for the ash from the coke has been made. Or one of the three may be a limestone or a silicious flux ; it need not necessarily contain iron.

Then let it be required to have n parts of iron per hundred of the charge, and let a_1, a_2, a_3 , be percentages of iron in the ores, and b_1, b_2, b_3 , percentages of deficiency (or excess) of silica in the same, and x, y, z , the number of parts required of the component ores per hundred of the charge.

Thus—

	FeO		Silica.
x	$\left[\begin{array}{c} a_1 \\ a_2 \\ a_3 \end{array} \right]$	$\begin{array}{c} + \\ - \\ + \end{array}$	$\left[\begin{array}{c} b_1 \\ b_2 \\ b_3 \end{array} \right]$
y			
z			

Then—

$$(1) \quad x + y + z = 100$$

$$(2) \quad \frac{xa_1 + ya_2 + za_3}{100} = n$$

$$(3) \quad xb_1 - yb_2 + zb_3 = 0$$

Solving these simple equations, the number of parts of each component required to satisfy the desired conditions of the charge is at once formed.

If it is desired to produce a more acid or a more basic slag, it is only necessary that the scale b be replaced by one the length of whose gradations are one half (for bi-silicate slag) or twice (for bi-basic slag) that of the normal scale.

A simpler form of the rule can be made by drawing the lines AB, AC, AD, AE, as before, upon a sheet of card, and then setting out a scale of equal parts upon the datum line AB, and providing a loose strip of card, one edge of which is graduated to the same scale, taking care, in using the scale, to keep it at right angles to the line AB. This is, in fact, the equivalent of a set of Professor Balling's diagrams, reduced to one scale, and brought to a common centre.

Mr. A. Wingham * has also devised an excellent slide rule for the same purpose as the foregoing appliance, and by it the additions, as well as the multiplications, are mechanically performed, provision being made for all the ordinary constituents of slags.

Classification of Metallurgical Processes.—Metals may be extracted from their ores by the following methods:

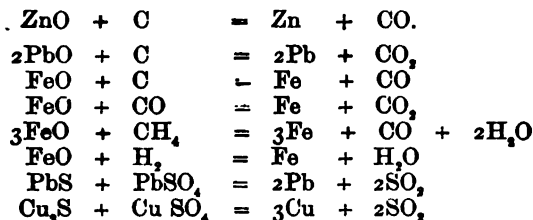
1. By *liquation*—that is, a separation of the easily fusible metals or metallic compounds from the infusible ones, or the gangue, at a low temperature, by taking advantage of the different melting points. In this way, bismuth and sulphide of anti-

* *Journ. Iron and Steel Inst.* part i. 1892, p. 233.

mony are obtained, and argentiferous lead is separated from copper.

2. By *distillation* and *sublimation*—that is, heating the ore, until the metal is driven off in the form of vapour, and condensed in a liquid or solid state. Mercury is extracted from its ore by distillation, and arsenic is obtained by sublimation.

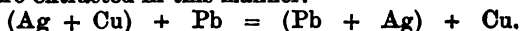
3. By reduction of metallic oxides at a high temperature. In the case of metals possessing a slight affinity for oxygen, the reduction may be effected by merely heating the oxide, whereby it splits up into metal and oxygen. The reduction is usually effected by heating the oxides with carbon or other substances possessing a greater affinity for oxygen than is possessed by the metal. In addition to solid carbon the substances used are carbonic oxide, marsh-gas, and hydrogen, as well as sulphur in the reverberatory-furnace processes for extracting copper and lead. The reactions are shown by the following equations:—



4. By decomposing metallic sulphides by means of iron at a high temperature. Lead and antimony are extracted from their ores in this way, the equation in the case of lead being—



5. By extraction by means of molten lead. The precious metals are extracted in this manner.

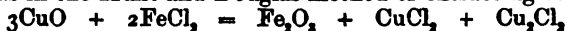


6. By extraction by means of molten zinc, as in the extraction of silver and gold from lead by the Parkes process.

7. By extraction by means of mercury in the cold. This process is known as *amalgamation*. It is used for extracting silver and gold from their ores, the mercury being subsequently driven off by heat.

8. By extraction in the wet way and subsequent precipitation, as metal or as oxide or sulphide. In some cases the compound is dissolved in acids, as in the separation of silver from gold, and in the extraction of copper and nickel. In other cases,

the metal is first converted into a chloride, which is dissolved in a solution of salt or of sodium hyposulphite, as in the extraction of silver by Augustin's process, or the metal is converted into a sulphate, which is dissolved in water, as in Ziervogel's process. The extraction may also be effected by treating oxides with salts, as in the Hunt and Douglas method of extracting copper.



9. By electrolysis, as in the deposition of copper.

10. By the action of highly oxidisable substances on metallic salts, as in the precipitation of gold from its solution as chloride by ferrous sulphate, or of aluminium from its chlorides by sodium.

11. By crystallisation, as in Pattinson's method of extracting silver.

Roasting and Calcination.—These terms are frequently used indiscriminately to indicate the operations of expelling water, carbonic anhydride, or sulphur from the ore, by heating the substance to a temperature below its melting point. The term calcination should be confined to the application of heat in the expulsion of carbonic anhydride or volatile matters, whilst the term roasting should be used in all cases where a chemical change is involved, resulting in the addition of an element.

Roasting is one of the most important of metallurgical processes. In the treatment of almost all ores it is required as a preliminary process to render them more porous and more suitable for the subsequent smelting, the success of which is dependent on the manner in which the roasting has been effected.

There are several kinds of roasting. An *oxidising* roasting is one in which the metalliferous substance is oxidised by heating it in contact with air. A *reducing* roasting consists in heating the substance in a reducing atmosphere. When it is required to obtain chlorides instead of oxides, the material is roasted with salt. This operation is termed a *chloridising* roasting. It is especially important in the treatment of silver ores. Under the action of a high temperature the salt acts on the sulphates present, and forms chlorides. Its action may also be due to the formation of chlorine by the action of silica and sulphuric anhydride on the salt, or to the evolution of hydrochloric acid, due to the presence of moisture in the atmosphere in which the material is being roasted. In some cases, as a preliminary operation for hydrometallurgical processes, it is necessary to conduct the roasting in such a manner that sulphates are formed. It necessitates a low

temperature and a limited supply of air. This operation is termed *sulphating* roasting.

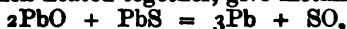
Oxidising Agents.—Atmospheric air is the simplest source of oxygen. The carbonic anhydride it contains may be neglected. Attention, however, must be paid to the aqueous vapour. Air, at the ordinary temperature, contains an amount of moisture equal to 0.0062 of the weight of dry air, or since water contains $\frac{8}{9}$ ths of its weight of oxygen, while dry air contains less than a quarter, it follows that the moister the air is the more oxidising it will be. The cooling action of water-vapour, however, counteracts the advantage derived from its excess of oxygen. Moist air is consequently useful only when the hydrogen it contains is set at liberty during the reactions and is free to combine with sulphur or certain other metalloids. Air is employed at the ordinary pressure or at the pressure of several atmospheres, for the temperature of combustion increases with the pressure.

Water is an active oxidising agent in the case of certain metals which have a strong affinity for oxygen; but in other cases its oxidising action is sensible only at a high temperature. The decomposition of water absorbs much heat, and aqueous vapour can therefore be employed only as an oxidising agent when its cooling effect is desirable, as in the refining of iron. Aqueous vapour is also used for separating zinc from lead. In passing steam over sulphides of oxidisable metals at a red heat the sulphur is eliminated as sulphuretted hydrogen, while the metal is oxidised. This reaction is employed in the roasting of sulphides of iron, and in the treatment of sulphides, arseno-sulphides and antimonio-sulphides of copper and silver.

Metallic oxides are frequently used as oxidising agents. Oxides of manganese, iron and lead are those most generally employed. Oxide of copper is used more rarely. Manganese peroxide is occasionally useful in the oxidation of impurities in metals. Ferrous oxide, or ferrous silicate, acts as a carrier of atmospheric oxygen. When ferrous silicate, containing less than 30 per cent. of silica, is exposed in a molten state to the action of air, the iron in excess gradually becomes oxidised, and crystals of magnetic oxide are formed. These render the silicate less fusible, and fall by their superior density to the bottom of the mass. Sometimes, as when such a slag covers a bath of impure metal, the magnetic oxide thus formed gives up its excess of oxygen to the elements in the metal to be refined, and again becomes ferrous oxide, and thus acts as a carrier of atmospheric oxygen to the carbon which has to be oxidised. An illustration of this is afforded by a stage

of the puddling of iron, a process which is conducted in the presence of a layer of ferruginous cinder.

Lead oxide is an energetic oxidising agent on account of its being readily reducible to the metallic state. It is, however, expensive, and yields but 7 per cent. of oxygen. Lead oxide and lead sulphide, when heated together, give metallic lead—



Oxides of copper and antimony serve as oxidisers in the treatment of these metals. In heating together the sulphide and oxide of copper, copper is obtained. Potassium and sodium nitrates are employed in refining silver and antimony, and in the "Heaton" process sodium nitrate is employed to convert phosphorus and vanadium in certain varieties of pig-iron into sodium phosphate and vanadate.

Metallic sulphates are often used as oxidising agents, the sulphate oxidising the sulphide and reducing the metal. In the case of iron in the blast furnace, carbonic anhydride, as is shown in the following chapter, also acts as an oxidiser.

Reducing Agents.—When a metal is separated from a state of chemical combination, it is said to be reduced, and the process of separation is termed *reduction*. The agents employed for this purpose are mainly carbon and hydrogen, or their compounds. Occasionally, however, the metallurgist makes use of iron, manganese, lead, or of sulphides and arsenides. The efficacy of a reducing agent depends on the absence of oxidised or inert elements. Thus, on account of the water and oxidised compounds they contain, wood, peat, and lignite are less energetic as reducing agents than coal. Similarly, coals rich in carbon are more valuable as reducing agents than coals rich in oxygen.

Carbon can take up $1\frac{1}{3}$ rd or $2\frac{2}{3}$ rds of its weight of oxygen according to the oxide in whose presence it is used, to the temperature at which the reduction is effected, and to the relative proportion between the oxygen to be removed and the carbon employed. In the first case carbonic oxide is formed, and in the second carbonic anhydride. The reduction of metals, of which the oxides are easily reduced, such as lead and copper, is complete even if carbonic anhydride alone is formed. In the case of iron, however, total reduction is not possible unless carbonic oxide is present in excess, on account of the oxidising action of carbonic anhydride. Indeed, a mixture of equal volumes of carbonic oxide and carbonic anhydride will not reduce iron oxides below ferrous oxide. This is also true of manganese oxides.

Reduction by solid carbon is slow, and is effected merely by

cementation, that is, by a gradual transmitting action, if carbonic oxide is not formed. This gas is the most important reducing agent. It penetrates to the centre of the oxidised substance, absorbs its oxygen, and is converted into carbonic anhydride. In this way 1 part by weight of carbonic oxide gives 1.57 parts of carbonic anhydride. Besides this, Gruner* and Sir Lowthian Bell† have shown that, even at low temperatures, carbon, in the presence of iron, separates out from carbonic oxide,



and has a powerful reducing action. It continuously converts carbonic anhydride into the lower oxide (see p. 243). Hydrogen is a powerful reducing agent, but is only used incidentally.

In addition to the above-mentioned reducing agents, metals and metalloids are sometimes used to remove oxygen. Thus, iron deoxidises the salts and oxides of copper, of lead, and of mercury, and sodium liberates the metals magnesium and aluminium, from their haloid salts. Sulphides and arsenides are also employed. Thus, sulphides of iron and zinc separate copper from certain slags. Silicates of iron and zinc are formed, while sulphur retains the copper in the regulus.

Chemical Agents.—Certain sulphurising agents are employed in metallurgical processes. These are specially useful in the treatment of silver and copper. The agents are iron or copper pyrites, barium or calcium sulphates, and, less frequently, metallic sulphides. Nickel and cobalt behave with regard to arsenic as silver and copper do in the case of sulphur. These metals may be protected, by means of their affinity for arsenic, from the scori-fying action of silicates.

Chlorine is largely used in the treatment of gold and silver ores. It is employed in the gaseous state or in the form of alkaline hypochlorites. The perchlorides of iron, copper, and mercury act as chloridising agents by being converted into lower chlorides. They are obtained usually by the direct action of hydrochloric acid on peroxides. Iodine is used in the metallurgy of silver, and bromine in that of gold.

The agents employed for effecting the solution of metallic substances are very varied. The most important solvent is water, which is used for dissolving sulphates of iron, copper, and zinc. Other salts are dissolved by salt solutions; thus, chloride of silver is dissolved by an aqueous solution of sodium chloride.

* *Ann. de Chim. et de Phys.*, 4th Series, vol. xxvi. (1872), p. 5; *Traité de Métallurgie*, vol. i. (1875), p. 172.

† *Chemical Phenomena of Iron Smelting*.

Calcium chloride, sodium hyposulphite, and ammonium carbonate are also used. Compounds of sulphur, oxygen, and calcium are now largely used in the metallurgy of silver. Metallic oxides are dissolved by acids, gold and platinum are dissolved by aqua regia, and in the amalgamation of gold and silver, mercury is the solvent employed.

In metallurgical processes there are scarcely any limits to the use of ordinary chemical reagents beyond those imposed by the price of the material.

CHAPTER VII.

FURNACES.

Materials used in the Construction of Furnaces.—In addition to the ordinary building materials used for the exterior portions of furnaces, refractory bricks and materials are required for the interior where a high temperature and the scouring action of metallic oxides have to be resisted. These materials may be used either in the natural state or as bricks. Of the natural materials, sandstones are most largely employed, the best varieties being those in which the quartz grains are cemented by a siliceous material. In the form of quartz, silica is able to resist all temperatures except that of the oxy-hydrogen blowpipe. Coarse-grained sandstones, such as millstone-grit, are frequently advantageously used. The Dinas rock found in the Vale of Neath, South Wales, is an example of this type. It usually contains 98 per cent. of silica. The pulverised rock is mixed with a little lime or clay to make it cohere, and is pressed into bricks. These resist a very high temperature, and are especially useful for the arches of reverberatory furnaces, as they expand with heat. Their composition, however, does not enable them to resist the action of metallic oxides. In steel-melting furnaces, where Dinas bricks are used, the tie-rods must be slackened as the heat increases, and tightened when the furnace subsequently cools. Silica bricks should be set as hot as possible, and the temperature of the furnace gradually raised. Ganister is a siliceous material, somewhat similar to the Dinas stone, found in the lower coal-measures of Yorkshire.

There are three classes of refractory materials :—

1. *Acid*, such as Dinas stone and ganister.
2. *Neutral*, such as graphite, chrome-iron ore, and fire-clay.
3. *Basic*, such as bauxite, dolomite, and magnesite.

Basic materials are now largely used. Bauxite is used for resisting metallic oxides, and for that reason it is used for lining Siemens furnaces. It is first calcined with 3 per cent. of

arenaceous clay mixed with a little graphite. It is essentially a hydrated ferric aluminate, and has the following composition :—

Al_2O_3	...	Fe_2O_3	...	SiO_2	...	H_2O
50 to 60		24 to 25		3 to 5		10 to 15

The use of basic refractory materials has been rendered necessary by the extension of the basic Bessemer process. Formerly the Bessemer converter, capable of holding 5 tons of metal, was invariably lined with ganister or Dinas stone. With such a lining, however, it was impossible to get rid of the phosphorus in the iron, whilst with a basic lining this is easily accomplished. Lime is one of the most refractory substances known, but it cannot be used on account of its readiness to become hydrated, and consequently to disintegrate. Magnesia, too, does not appear to answer well; but magnesite gives excellent bricks. Its great cost, however, precludes its general adoption. The mixtures of lime and magnesia, obtained by heating dolomite, give the most satisfactory results. Coated with tar, they are easily protected from moisture, and the proportion of silica they contain is considered advantageous. A refractory material of this kind containing

MgCO_3	...	CaCO_3	...	SiO_2	...	$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3$
88		7		4		1

is largely used. The slag obtained from basic refractory materials in the Bessemer converter is being largely used as a fertilizer for agricultural purposes on account of the phosphorus it contains. Some 400,000 tons of it are annually used in Germany.

Fire-bricks are mostly made of fire-clay, mixed with quartz, burnt clay, or pulverised refractory materials that have previously been used. The admixture of graphite is not so usual for fire-bricks as for the refractory crucibles in which metals and alloys are melted.

Fire-clays consist essentially of hydrated aluminium silicates, having the following composition :—

SiO_2	...	Al_2O_3	...	H_2O
50 to 55		30 to 35		10 to 15

When lime, magnesia, potash, or soda are present in quantities exceeding 1 per cent. the clay becomes fusible. In aluminous clays less than 0.7 per cent. of these oxides does not depreciate their refractory value. As a rule, a small amount of these oxides or of ferrous oxide is sufficient to condemn a clay. Thus ordinary shale fuses at a comparatively low temperature, on account of its large percentage of alkaline oxides and ferrous oxide.

The plasticity of clays depends upon the fineness of the particles

and the amount of water present. When calcined, clays cease to be plastic when moistened, on account of the molecular alteration brought about by the calcination. Fire-clays contract when heated, even after all their combined water has been driven off. Heating, however, up to 100° does not affect plasticity; it merely drives off the hygroscopic water. The quality of the clay is largely dependent upon the free silica it contains. Windsor fire-bricks, which may advantageously be used when the temperatures are not high, are made of a mixture of sand and fire-clay in equal proportions.

The mortar employed for setting fire-bricks is prepared from the same materials as the bricks themselves, or from good clay. Lime mortar must not be employed for work that has to support high temperatures.*

Crucibles.—For special metallurgical purposes, in the furnaces are placed crucibles (manufacture of cast steel, zinc, smalts, antimony), or tubes or muffles (Belgian and Silesian methods of smelting zinc), or retorts (arsenic smelting). Pear-shaped vessels, open at both ends, termed aludels, are used in mercury smelting. As most of these vessels must be made of refractory materials, they may be conveniently discussed here.

Crucibles are required to resist (1) high temperatures; (2) alternating temperatures; and (3) the corroding action of metallic oxides. They must also not be brittle or "tender" when hot. They may be made of clay, graphite, gas-carbon, and many other materials, according to requirements. When made of clay, two-thirds are raw clay and one-third is burnt clay, or pulverised material obtained from old but cleaned pots. By this addition, contraction on drying is avoided.

In order to test fire-clay, a piece is fashioned with sharp angles, dried, and exposed to a white heat in a muffle; it is then examined to see if the edges have fused. A similar test should be made in a reducing atmosphere, the test-piece being placed in a crucible packed with charcoal. In order to test the resistance of a crucible to corrosion, it may be half filled with copper, which is then melted, and a little borax inserted so as to just form a ring round the edge of the molten metal and yet leave the centre free for oxidation. The borax will absorb the oxide and rapidly corrode the crucible unless it be of excellent quality. The behaviour of the crucible under the weight of the copper melted indicates the other qualities of the crucible. In selecting clay for crucibles, special care must be taken that neither iron pyrites nor more than a

* Snelus, *Journ. Iron and Steel Inst.*, 1875, p. 513.

minute percentage of potash or soda is present. A small quantity of lime is of no importance.

The so-called plumbago crucibles are made of clay and graphite, in the proportion of 51 of the former to 49 of the latter. Only certain varieties of graphite can be used for crucible-making, the texture being of great importance. This can only be determined by experiment. Ceylon graphite contains 79.4 per cent. of carbon, 15.5 per cent. of ash, the remainder being volatile matter. The ash may contain as much as 12 per cent. of ferric oxide, which must be removed by treatment with sulphuric acid. The graphite is picked, ground, sifted, and mixed with the fire-clay, and left for some time to "mellow" after it has been kneaded damp. The crucibles are moulded, dried, and then burnt in kilns. Obviously, an oxidising atmosphere must always be avoided. In order to prevent absorption of moisture and salts, as in cases of shipment, and to enable rapid alterations of temperature to be better withstood, the finished crucibles are dipped in milk of clay, dried, glazed, and then dipped in tar. Crucibles made in this way by the Patent Plumbago Crucible Company, of Battersea, will stand 40 meltings of gold without sensible deterioration.

The pots used in the chlorination process for parting gold and silver are soaked in borax solution, dried and heated. The borax then melts and clogs the pores, and prevents the escape of the silver chloride, which is very fluid.

Classification of Furnaces.—The words *hearth*, *forge*, and *furnace* are applied to structures in which ores or metals are submitted to high temperatures. A furnace is composed of an interior part, of fire-resisting materials, and an exterior part built for the purpose of consolidating the interior structure. Furnaces may be divided into two classes—(1) those in which the charge and fuel are in intimate contact, there being no independent hearth or fireplace, and (2) those in which the fuel and ore are kept separate, the fuel being burnt in an independent hearth. The first class of furnaces may be sub-divided, according to their height and construction, into *hearths* and *blast-furnaces*; the former are imperfect appliances that usually do not work continuously, whilst in the blast-furnace the action is continuous. The second class is sub-divided into (a) *reverberatory-furnaces*; a group in which gas-furnaces may be included, and (b) *retort-furnaces*. In the former, the charge only comes in contact with the flame of the fuel, whilst in the retort-furnaces it does not come into contact with the combustible gases of the fuel at all, but is separated from them by walls that merely

transmit the heat. These walls usually form part of separate closed vessels, crucibles, muffles, or retorts, but occasionally they are part of the furnace itself. In this classification, the Bessemer converter is omitted. It cannot be classed as either a hearth or blast-furnace, but it may be described as a vessel usually pear-shaped, in which the impurities contained in the metal treated constitute the fuel which is burnt by a forced current of air. Furnaces may be further divided into those worked by means of a natural current of air, and those worked by a forced current of air. The classification of furnaces may then be summarised thus:—

I.—HEARTHES.

(a) Worked by means of a natural current of air. 1. Roasting hearth (piles, stalls, pits, kilns); 2. Liquation-hearth (hearth for liquating argentiferous copper).

(b) Worked by means of a forced draught (the smith's forge, iron refinery).

II.—SHAFT-FURNACES.

(a) Draught-furnaces (iron ore calciners).

(b) Blast-furnaces (iron blast-furnace, Raschette-furnace, Pils-furnace, cupola-furnace).

III.—REVERBERATORY-FURNACES.

(a) Worked by means of natural draught (puddling-furnace).

(b) Worked by means of a forced draught (cupellation-furnace).

IV.—CLOSED-VESSEL FURNACES.

May be divided, according to the form of the vessel employed, into—

(a) Crucible-furnace (Deville blast-furnace).

(b) retort-furnace (for zinc, mercury).

(c) tube-furnace (for bismuth).

(d) muffle-furnace (for arsenic).

or, according to the process carried out in it, into—

(a) smelting-furnace (ordinary assay-furnace).

(b) roasting-furnace (arsenic).

(c) liquation-furnace (bismuth).

(d) distillation-furnace (zinc, mercury).

(e) sublimation-furnace (arsenious acid).

(f) cementation-furnace (cement steel).

V. ELECTRICAL FURNACE.

In which the combustion of carbon need not, even indirectly, produce heat.

Whether the furnace is worked by natural or forced draught, the general principles involved in the combustion of fuel apply.

The fuel employed in either case may be the same, but the products of its combustion may be widely different. The form and dimensions of the furnace will obviously give rise to a very varied series of results; since on them depends the amount of fuel that can be burnt in a given time, and the degree of perfection of the combustion that can be attained, the temperature actually engendered being dependent on the calorific power of the fuel. There may, in fact, be any variations in heat-units between 2473 and 8080 *calories*, the calorific powers of carbon when burnt to carbonic oxide and to carbonic anhydride respectively. In a furnace without an independent hearth, the most important part is that in which the work is principally done. This may be conveniently localised as the zone of combustion. Thus, as Gruner expresses it, for a given fuel burnt in a certain way, the heat developed will simply be proportional to the weight of fuel burnt, whilst the temperature depends on the rapidity of combustion—that is, on the ratio between the volume of the zone of combustion and the weight of coal or coke burnt in an hour. The smaller this ratio, the higher the temperature will be.

In order to show how varied the conditions may be, the following two cases may be cited:—(1) A vat-shaped furnace, such as is used in the Cleveland district for calcining ironstone with a natural draught of air. One hundred and fifteen tons of iron carbonate are calcined in twenty-four hours with a consumption of 4 tons 12 cwt. of coal. The height of the furnace is 33 feet, and its total internal capacity is 8000 cubic feet; but the work of the furnace—namely, that of driving off carbonic anhydride and moisture from an iron ore, is not confined to a limited zone; indeed, the volume of this zone of combustion may be taken to be 1400 cubic feet. Compare this with (2) a modern blast-furnace, such as that used at the Ormsby Ironworks, Middlesborough, a furnace to which reference will again be made in dealing with the blast-furnace. The height of the furnace is 76 feet, and its out-turn is 2453 tons per month, or about 80 tons of pig-iron in twenty-four hours. In this case heated air is driven in, a course which is necessary in order to overcome the resistance of the superincumbent and partially fused mass of ore, fuel, and flux, and the result is that the combustion of the fuel is more or less limited to an intensely hot zone of combustion, the capacity of which does not exceed 200 cubic feet.

Furnaces with independent hearths are usually reverberatory-furnaces, although there are cases in which vat-shaped furnaces are supplemented by fire-grates, which are usually symmetrically arranged round the base. The object of isolating the fuel from

the ore is in order to prevent chemical action of a kind that is not wanted, and generally to enable the nature of the products of combustion admitted into the furnace to be controlled. It would be useless, for instance, to admit torrents of carbonic oxide into a furnace where an oxidising action was wanted, and conversely the predominance of an atmosphere of carbonic anhydride would be fatal to a reducing action.

In France it is usual to consider a reverberatory-furnace as consisting of a grate to hold the fuel, and the "laboratory" portion in which a given operation is conducted. The nature of the operation may be infinitely varied, and the temperature of the laboratory may vary from the dull red heat required for roasting pyritic ores to the intense heat required for melting steel. Obviously, the dimensions of the grate in relation to those of the laboratory will vary considerably, and Gruner has given valuable data for determining what these ratios should be. He shows, for instance, that in conducting certain typical operations, it is necessary to burn in an hour the following amounts of fuel, in lbs. for every square foot of grate area:—

Furnace.	Lbs. per sq. ft.
Furnace for roasting sulphides	3 to 8
Fires for stationary boilers	8 to 20
Furnaces used in smelting lead ores	12 to 16
Furnaces for copper smelting	15 to 30
Puddling furnaces	20 to 30
Steel melting furnaces	41 to 81
Locomotive fires	81 to 102

Lastly, Gruner has given the relation between the volume of the laboratory portion of the furnace and the amount of coal or coke burnt in an hour on the grate, distinguishing between furnaces in which the heating has to be slow or rapid. In the former case, the volume of the laboratory part for every cwt. of coal burnt in air is—

	Cubic feet.
In brick-making	1794
roasting copper ores	538
reducing zinc	101

whilst in furnaces with rapid heating, it is—

	Cubic feet.
In fusion of copper regulus at Swansea	50
ordinary puddling	17½ to 20
steel melting on the bed of a reverberatory-furnace	2½ to 3½

1. **Hearths.**—A hearth is a low furnace in which the material to be treated is exposed to the direct action of solid fuel. Heaps,

stalls, and kilns for roasting ore, are also included in this category, as the action of the fuel is the same. Consequently, hearths are not necessarily enclosed furnaces, but may exist without the aid of any brickwork at all. The pyramidal heaps, in which the roasting of copper ores is effected, are free or unwallled, about 30 feet square at the base, and built upon level ground. A bed of wood, about 1 foot in thickness, is formed, and on this alternated layers of ore and charcoal are piled to the vertical height of 10 feet. Some ironstone from the coal-measures may be roasted in heaps without the addition of fuel. The proportion of bitumen in the copper shale of Mansfeld is almost sufficient for its calcination. With sulphuretted ores, a bed of fuel is used, the burning sulphur keeping up the roasting temperature. Coke-ovens may also be classed as hearths, and so also may the primitive liquation-hearth formerly employed for separating easily fusible constituents out of metallic mixtures.

Hearths worked by means of a forced current of air may be employed for melting or for heating a substance to a very high temperature without altering its state of aggregation, as in welding and forging metals that are not readily fusible.

An example of this class of hearth is the refinery formerly largely used in the manufacture of malleable iron. It consists of a rectangular hearth, provided with inclined tuyeres, through which air is blown upon the surface of the molten iron, so that the silicon in the iron is oxidised, forming with a portion of the iron a fusible ferrous silicate. This process is now unimportant, being confined to forges in a few localities making special qualities of malleable iron.

Further examples are afforded by the shallow hearths used for lead-smelting. In the North of England, a furnace of this kind, known as the *ore-hearth*, is often used. It consists of a cubical chamber, about 22 inches side, lined with cast-iron. In the back wall is fixed a tuyere for the introduction of the blast. In front is the work-stone, which is placed at a slight inclination to the bottom of the hearth. The melted lead flows from the hearth down an oblique channel in the work-stone to a lead pot placed before the work-stone. The operation lasts about twelve hours, the production being 1 to 1½ ton of lead. Peat was formerly used as fuel, but it has now been abandoned and coal is generally used.

In hearths and kilns of this class, the introduction of cold material renders the combustion of the fuel, whether gaseous or solid, more or less imperfect, so that the products of combustion contain an inordinate amount of unburnt gases, especially of carbonic oxide. As a rule, in a kiln the position of the zone

of combustion is fixed, but it occurred to Hoffmann,* a German architect, to devise a kiln in which the position of the zone

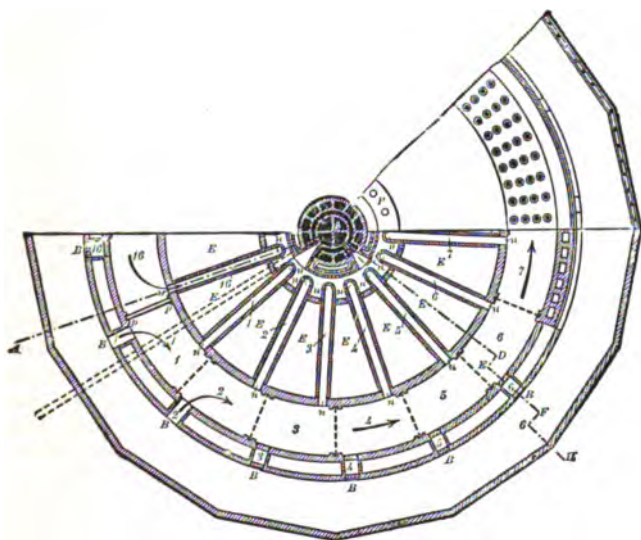
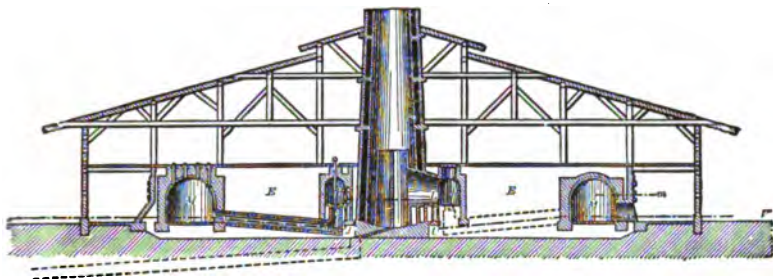


FIG. 54.

of combustion can be varied at will, and he thus succeeded in effecting a considerable economy of fuel. In an ordinary kiln

* *Annales des Mines*, 6th Series, vol. xx. (1871), p. 325.

there is a continuous ascending column of gas, and a descending column of solid material. In the Hoffmann kiln, on the other hand, the solid material remains stationary, while the gaseous current alone moves. The kiln may be either circular or oval in section, the circular being the more usual form. This is shown in Fig. 54. It consists of a circular tunnel, *MM*, which can be divided into any number of compartments, twelve or sixteen being the usual number. These compartments are, however, in direct communication with each other, except at one point, where an iron plate, *pp*, placed across the tunnel, interrupts the continuity. This plate may be inserted through the roof of the tunnel down grooves, *nn*, provided for its reception, in the walls. Each space between two sets of grooves is provided with an internal flue, *E, E*, which, by the removal of a damper, can be placed in communication with a central chimney, and each space has also a door, *BB*, in the outer wall. Only two of these doors are open at a time. The whole of the tunnel is kept full of material (ores to be calcined, or bricks to be burnt), except one compartment, which is always empty. The position of the empty compartment varies from day to day. Let the plate occupy the position, *pp*, shown in Fig. 54. The newest material has been charged in behind it into compartment 16. Air enters in front of it through the open door of the empty compartment No. 1, and through the door, also open, of the next compartment, which contains finished material that has been longer in the furnace than the rest, and has but little heat to give up to the in-coming current of air. This current is drawn by natural draught round the entire tunnel, and can only enter the chimney through one or more of the flues that have been opened behind the plate. After an interval of twenty-four hours from the last charging, the position of the iron partition is shifted to the next groove to the right, the compartment No. 1 is filled, and the one, No. 2, in front of the plate is emptied. Thus, new material is continually kept behind the plate, and finished material in front of it. Air entering comes in contact with material which gradually increases in temperature, for it will be obvious that the position of the hottest part of the furnace must be continually travelling round the circle, and that in a number of days, corresponding with the number of compartments, the zone of combustion will have travelled completely round the circuit. The air and the material to be treated enter and leave the furnace in a cold condition, so that there can be no waste of heat, provided that the adjustment of the dampers in the flues through which the gases pass to the chimney, is carefully effected. In order to remedy local irregu-

larities of combustion, air may, if necessary, be admitted through suitable orifices in the roof.

The volume of each compartment may vary from 282 to 1765 cubic feet. In order to facilitate charging and to secure perfect uniformity of temperature, the height of the tunnel should not exceed 9 feet.

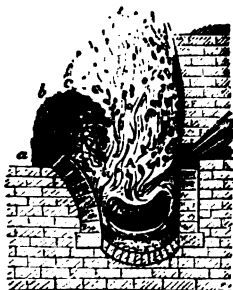


FIG. 55.

In Catalonia, a low hearth, the Catalan furnace (Fig. 55), is still occasionally to be met with. It is used for the production of malleable iron direct from the ore. It is made of blocks of cast-iron and has a sandstone bottom. The tuyere is made of sheet copper. The blast is supplied by a water-blowing machine, or *trompe*, which may be made from a hollow tree trunk, 15 feet high, at the top of which is a water-

box with a plug. The water falls down the pipe into the wind-box, carrying air with it, and causing a pressure of $1\frac{1}{2}$ to 2 lbs. per square inch in the hearth.

2. **Shaft-furnaces.**—In all the members of this group the fuel and ore are charged into a common receptacle, the axis of which is vertical. Certain of them, as the kilns in which limestone or ore is calcined, are worked by a natural current of air, the furnace itself forming a capacious chimney.

The form of these furnaces is very varied, according to the nature of the ore and of the fuel employed. Furnaces of this kind may be egg-shaped, cylindrical or conical. Small kilns with circular horizontal section effect the most uniform roasting, give rise to the least loss of heat by radiation, and wear well. They, however, necessitate the use of expensive bricks of special shape. The height is dependent on the size of the pieces and on the fusibility of the ore. The width is dependent on the quantity of ore to be roasted. In large kilns of circular section it is difficult to maintain a uniform temperature. Large kilns have consequently an elliptical or rectangular section. In the latter case the corners are rounded off.

The best examples of this type of furnace are afforded by the kilns employed for calcining iron ores. One of the best forms is that of Gjers (Fig. 56), which is extensively used in the Cleveland district. The drawing, to the scale of 10 feet to the inch, shows this kiln partly in elevation and partly in section. The body is of fire-brick cased with malleable iron plates. The bottom of the brickwork rests on a cast-iron ring, *a*, and the whole is

supported by cast-iron pillars, *b*, leaving a clear space between the bottom of the kiln and the floor. The latter is covered by iron plates, *c*, on the centre of which is fixed a cast-iron cone, *d*, 8 feet in height and 8 feet in diameter at the base. This causes the descending roasted ore to pass outwards. Fresh ore and coal

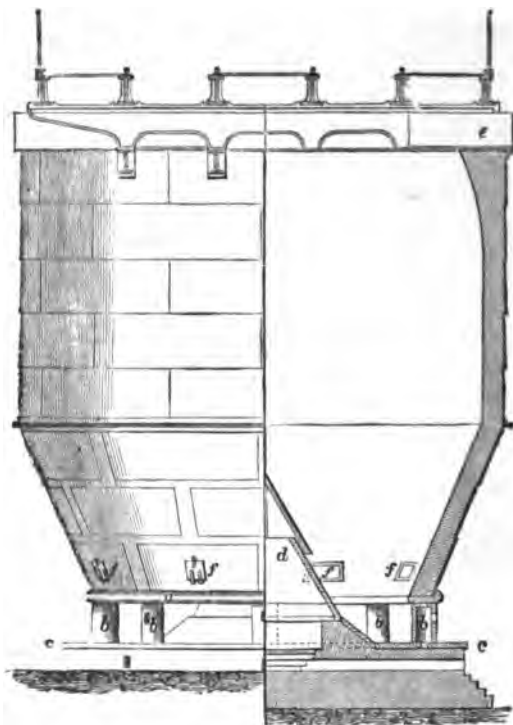


FIG. 56.

are constantly being added from the filling gallery, *e*. Around the lower tier of plates are openings, *f*, which are usually closed by doors, but which serve for the admission of air or tools in case of the ore becoming clotted. These kilns are usually 33 feet in height, 24 feet in diameter at the widest part, and have a capacity of

8000 cubic feet. They calcine 800 tons of iron ore per week, the consumption of coal amounting to 1 ton for 25 tons of ore.

In Styria, kilns are used provided with step-grates. A kiln of this kind is shown in Fig. 57, in vertical section drawn to the same scale as the preceding figure. The masonry, *a*, is of rubble-work, the lining, *b*, of the kiln is of fire-brick, the grate, *c*, and the bottom, *d*, are of cast-iron.

In all blast-furnaces carbonic oxide is the main reducing agent, but in certain forms, such as those employed in the smelting of lead ores where only moderate temperatures are required, care is taken that the atmosphere is not too reducing, or intractable

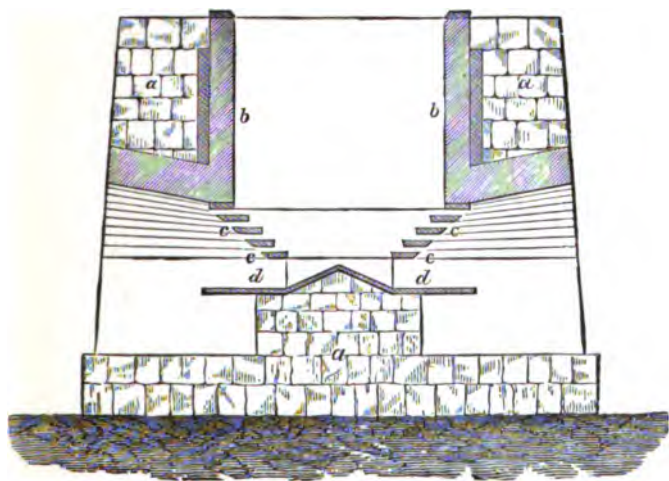


FIG. 57.

masses of iron will be produced which will impede the action of the furnace. The generation of carbonic oxide in front of tuyeres supplies the heat to melt the slag and metal, whilst the gas itself is the reducing agent throughout the process. Usually by far the most important point to consider is the temperature actually attained in the zone of combustion—that is to say, the portion of the furnace near the tuyeres where the fuel is actually burnt. The temperature will depend on the relation between the volume of the zone of combustion and the weight of fuel burnt in an hour. The smaller this ratio is, the higher the temperature will be.

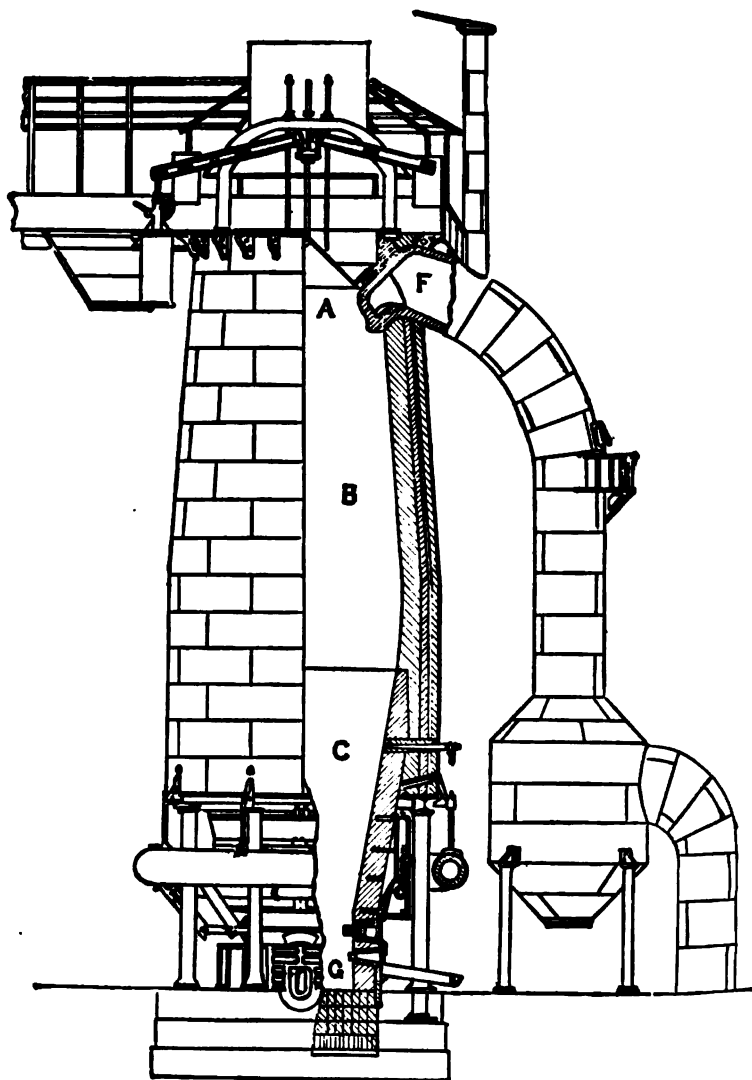


FIG. 58.

The most important member of the group of furnaces without separate hearth is the blast-furnace. As its name implies, it is worked by a forced current of air supplied by a bellows or by blowing-engines. The blast-furnace in which pig-iron is made is shown in Fig. 58. In former times charcoal was exclusively the fuel employed, whilst at the present time coke is mostly used. Raw fuel (coal or anthracite) is only adopted in special cases. The modern blast-furnace, in which coke is used as fuel, is 70 to 80 feet in height, some of the larger examples attaining to 100 feet. Charcoal blast-furnaces are considerably smaller. Formerly, the blast-furnace was a heavy conical mass of masonry some 30 feet in height. It is now a much lighter structure, formed of a wrought-iron casing lined with brickwork. In order to distinguish it from the older forms, it is termed a cupola blast-furnace. In the upper opening, or throat, fuel or ore are charged, being allowed to fall into the furnace, usually through some form of appliance for distributing the charge. In the lower narrow portion of the furnace, highly compressed air is forced through a number (usually five to eight) of horizontal nozzles or tuyeres arranged in a circle. When the blast is previously heated, the water-tuyere is always employed. It consists of a hollow truncated cone, through which a current of water circulates. In the space in front of the tuyeres, the consumption of the fuel is effected, which is already highly heated in its descent through the furnace, and a temperature of more than 2000° is obtained. The plane in the blast-furnace where the greatest diameter is reached is termed the *boshes*, and the cylindrical portion at the base is the *hearth*, G, in which the molten material collects. The top of the furnace is surrounded by a charging gallery, and is usually covered in by an iron cup and cone, A, the latter of which may be lowered by a counterpoise and winch or by an hydraulic cylinder, when material is to be charged in, the waste gases passing through a side tube, F, whence they are led to the stoves for heating the blast, or are burnt under boilers. The stack is carried on an iron ring resting upon iron columns, the object being to have all the working parts of the furnace readily accessible so that they can be repaired from time to time. In front of the hearth an opening extends from the hearth-bottom to a little above the level of the tuyeres. The arch above this opening is called the *tymp arch*. The sides of the opening are prolonged outwards into a rectangular cavity, the *fore hearth*, which is bounded in front by a firebrick wall called the *dam*, carried up to the tuyere level and supported by a cast-iron *dam plate*, a semicircular notch, the *cinder notch*, in the top edge serving as a

passage for the slag. The *tap-hole* for withdrawing the molten iron is a narrow vertical opening in the bottom of the dam. The iron is run into sand moulds, forming *pigs* about 3 feet long.

A large modern blast-furnace produces 75 to 200 tons of pig-iron in twenty-four hours, whilst small charcoal blast-furnaces yield only 5 tons in the same time. Sometimes a furnace charge is obstructed in its descent. When the lower portion is melted, the obstructed un-reduced portion, or *scaffold*, is apt to give way suddenly and fall into the hearth.

Notwithstanding that iron-smelting dates from a very early period, the chemical changes that occur were very imperfectly understood in this country, until the subject was investigated by Sir Lowthian Bell* and Dr. C. R. Alder Wright.† The ores employed are usually subjected to a preliminary calcining, so as to convert ferrous carbonate into ferric oxide, to expel water, and to open out the texture of the ore. In some cases, however, the ore exists naturally as ferric oxide. The general composition of the ores chiefly used is:—

Red hæmatite :—Ferric oxide, with little or no earthy matter.

Magnetic ore :—Ferric and ferrous oxides, with earthy matter.

Spathic ore :—Ferrous carbonate and manganese carbonate, crystalline.

Clay ironstone :—Ferrous carbonate and much earthy matter.

Brown hæmatite :—Hydrated ferric oxide and earthy matter.

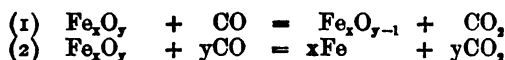
When the carbonate is not calcined before use, it soon loses its carbonic anhydride, leaving behind an oxide of iron. This occurs in the top portion of the furnace, so that virtually the ores used may be regarded as consisting essentially of some form of iron oxide with a varying amount of earthy matter. The fuel used is usually coke or charcoal. When raw coal is employed it is completely coked in the top portion of the furnace, so that the fuel burnt at the tuyeres is invariably carbon. This carbon is either burnt directly to carbonic oxide, or if burnt first to carbonic anhydride, it is immediately converted into carbonic oxide by the incandescent carbon. Most of the nitrogen of the blast remains unchanged, and any moisture in the blast is converted into a mixture of carbonic oxide and hydrogen. The amount of the latter necessarily varies with the hygrometric state of the atmosphere. The influence of the small quantity of hydrogen in blast-furnace gases is insignificant, since the gases issuing from the top of the furnace contain as much free hydrogen as that brought in by the

* *Chemical Phenomena of Iron Smelting*, London, 1872.

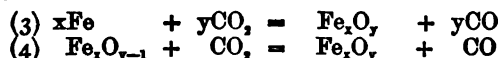
† *Proc. Roy. Inst. of Great Britain*, vol. vii. (1874), p. 248.

blast. Indeed, the liberation of hydrogen is injurious to the action rather than advantageous, for experience shows that the more moisture enters the furnace the more fuel is required to do the work. Virtually, therefore, the air passing into the blast-furnace becomes converted into a mixture of about two volumes of nitrogen and one volume of carbonic oxide. This ascends through the furnace and produces a number of complex chemical changes as it comes in contact with the ore. These changes are indicated by Dr. Alder Wright by the following equations:—

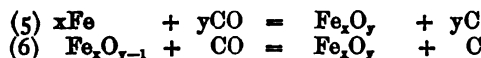
[A] Reduction of higher oxide to lower oxide and metal by gaseous carbonic oxide.



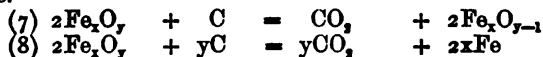
[B] Oxidation of metal and lower oxide to higher oxide by carbonic anhydride.



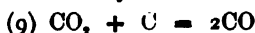
[C] Reduction of carbonic oxide to carbon.



[D] Reaction of reduced carbon on iron oxide forming carbonic anhydride.



[E] Reaction of carbonic anhydride on reduced carbon.



Although carbonic oxide exerts no action on ferric oxide at ordinary temperatures, yet its influence is appreciable at 150° , whilst in the converse changes [B] the oxidising effect of carbonic anhydride is scarcely appreciable at a temperature of 300° , but is noticeable at 400° and is very considerable at 600° . As regards equation (2) it may be remarked that it is impracticable to reduce the whole of the ferric oxide by means of carbonic oxide at any temperature short of a white heat. In fact, iron decomposes carbonic oxide at temperatures below this in virtue of equation (5).

At any given point in the blast-furnace, all the chemical tendencies thus indicated are at work simultaneously, with more or less vigour according to circumstances. The action actually taking place at this point is, therefore, that due to the single resultant of the various forces involved—namely, the iron-reducing ten-

dencies [A] and [D], the iron-oxidising [B] and [C], the carbon-reducing [C], and the carbon-oxidising [D] and [E] tendencies. Knowledge of the relative magnitude of these forces has been gained from the careful experiments of Sir Lowthian Bell and Dr. Alder-Wright. In tracing out the general chemical changes undergone by the oxide of iron, the furnace may be conveniently divided into three regions. In the uppermost region, tendencies [A] and [D] jointly are stronger than [B] and [C] jointly, and consequently rapid reduction of ferric oxide takes place. In this region, too, tendency [C] is more powerful than tendencies [D] and [E], and consequently carbon deposition takes place to a large extent. Here, too, the limestone flux is for the most part calcined into quicklime, raw coal, if used, is coked, and if iron carbonate is used, instead of oxide, it becomes converted into oxide, the reducing and carbon-depositing reactions going on simultaneously with the formation of the oxide.

In the middle region, the iron-reducing tendencies are almost balanced by the iron-oxidising ones, whilst the carbon-depositing tendencies are equalled by the carbon-oxidising ones. Here reduction takes place, but only languidly, the chief effect produced in passing through this region being an increase of temperature.

In the lowest region, the reduction of the residual iron oxide is completed chiefly through the agency of cyanides formed in the vicinity of the tuyeres; the reduced iron melts dissolving a certain amount of the finely divided carbon in contact with it, together with small quantities of silicon, phosphorus, and sulphur reduced by subsidiary reactions. The non-metallic constituents of the ore and the lime of the limestone also fuse, forming slag.

The nitrogen brought into the furnace acts solely as a diluent, except in the lower portions of the furnace. It has long been known that when nascent potassium or sodium vapour finds itself simultaneously in contact with carbon and nitrogen, the three elements combine, forming a metallic cyanide. The cyanide thus formed acts on the last portions of unreduced oxide of iron, converting it into metal and becoming itself changed to cyanate. This is probably decomposed with the formation of an alkaline carbonate and the elimination of nitrogen. The alkaline salts condensed in the upper portions of the furnace are again brought down to the level of the tuyeres as the materials sink. Consequently each particle of alkali metal does duty over and over again, the alkalis introduced in small quantities in the fuel accumulating in the furnace to a very large extent. As much as 4 cwt. of alkali metals and 2 cwt. of cyanogen per ton of iron made have been repeatedly found in the gases near the level of

the tuyeres. This concentration of alkali explains the fact that furnaces reduce more readily after they have been some time in blast.

In order to effect the smelting of iron, a definite amount of heat is required to perform the general work of the furnace, the various items in the appropriation of heat in an 80-foot blast-furnace, during the production of 20 cwt. of pig-iron from Cleveland ore being as follows:—

Constant requirements of furnace—

	Cwt. Heat-units.
Reduction of iron from ferric oxide . . .	33,108
Impregnation with carbon . . .	1,440
Reduction of phosphorus, sulphur, and silicon	4,174
Fusion of pig-iron	6,600
Radiation from walls of furnace . . .	3,658
Cooling tuyeres by water	1,818
Other sources of loss	3,202
	<hr/> 54,000

Variable sources of loss of heat—

Fusion of slag	16,720
Expulsion of carbonic anhydride from lime-stone	5,054
Decomposition of carbonic anhydride . . .	5,248
Decomposition of water in blast	2,720
Evaporation of water in coke	313
	<hr/> 30,055
Carried out by escaping gases	8,860
	<hr/> Total 92,915
Brought in by hot blast	11,919
	<hr/> Heat produced by combustion of coke 80,996

In order to produce this heat with a minimum expenditure of fuel, it is necessary that the whole of the carbon used as fuel should be oxidised to carbonic anhydride, an ideal that can only be realised in the reduction of lead oxide. The relative strengths of the forces involved in the nine reactions described are, in the case of iron ores, such that it is not possible to convert more than 35 or 40 per cent. of the carbon burnt into carbonic anhydride, the rest necessarily escaping as carbonic oxide. Consequently more fuel must be used to do the work of the furnace.

The most economical results are obtained when the ratio $\frac{\text{CO}_2}{\text{CO}}$ is greatest. This ratio, however, itself is modified by the temperature, the velocity, and the distribution of the gaseous current. Care must be taken to lessen, as far as possible, the amount of

the carbon burnt by the carbonic anhydride. The solid carbon is divided into two portions—one burnt in the zone of fusion, and the other in the zone of reduction. In the second case the reduction is effected with consumption of solid carbon, whilst in the former case, it is effected solely by the gases. The ideal case would be that in which carbon descends to the level of the tuyeres, and is there converted into carbonic oxide.

A convenient classification of blast-furnaces is that based on the ratio of the maximum diameter to the height. In this manner the following three classes may be distinguished:—

1. Squat furnaces, in which the height is less than, or equal to, three times the diameter, $\frac{H}{D} < 3$.

2. Ordinary furnaces, in which the ratio $\frac{H}{D}$ varies between 3 and 4, but is usually about 3.5.

3. Elongated furnaces, in which the ratio $\frac{H}{D}$ is greater than 4.

The following table gives comparative data of the dimensions and workings of ten typical blast-furnaces used for the smelting of iron:—

	Cubic Capacity.	Total Height.	Diameter at Hearth.	Diameter at Boshes.	Diameter at Throat.	Daily Out-put.	Time in Furnace.	Fuel per Ton of Metal.
	cub. ft.	ft. ins.	ft. ins.	ft. ins.	ft. ins.	tons.	hours.	lbs.
1	30,000	85 0	8 0	28 0	19 0	70	150	2308
2	18,000	80 0	11 0	22 0	16 0	270	21	1863
3	15,000	75 0	11 0	20 0	15 4	175	24	2116
4	14,000	75 0	8 0	21 0	14 0	107	36	2130
5	8,824	73 8	9 6	15 6	11 9	142	20	1943
6	6,676	72 4	8 6	15 0	9 6	114	19	1697
7	2,000	50 0	5 6	10 0	5 6	48	8	1870
8	1,872	49 8	4 6	10 4	3 4½	24	10	1365
9	1,235	37 3½	5 8	8 4½	3 1½	24	4	1653
10	1,000	37 6	5 6	7 0	3 0	20	7	1585

In the first six furnaces coke is the fuel employed, whilst charcoal is used in the last four. The names and situations of the furnaces are: 1. Newport, England; 2. Edgar Thomson "F," Pittsburgh, United States; 3. North Chicago, No. 6, Chicago, United States; 4. North Lonsdale, No. 3, Lancashire; 5. Union, No. 3 and No. 4; 6. Union, No. 2, Chicago; 7. Midland, Crawford County, Missouri, United States; 8. Treibach, Austria; 9.

Ferdinand, Hiefau, Austria; 10. Wrba, Eisenerz, Austria. The first four of these furnaces belong to the second class, in which $\frac{H}{D}$ is less than 4, whilst the last six are elongated furnaces in which the ratio $\frac{H}{D}$ is greater than 4. The following are examples of the first class, in which $\frac{H}{D}$ is less than 3.

	Name.	Cubic Capacity.	Height.	Diameter at Throat.	Diameter at Boshes.	Daily Out-turn.
		cu. ft.	ft.	ft. ins.	ft. ins.	tons.
11	Longwy, France .	14,656	65	13 6	23 0	40
12	Clarence (old type)	6,003	50	7 10	16 6	30
13	Thornaby " .	12,784	60	14 9	20 0	
14	Ormesby . .	40,984	90	15 9	30 0	

In furnaces of this type, the working is irregular on account of the contraction at the throat, which renders it difficult to apply any mechanical method of distributing the charge uniformly.

Mr. E. Walsh* shows that by placing the boshes, or widest diameter of the furnace, entirely within the zone of complete fusion a constant supply of fuel at the level of the tuyeres would be secured. He also concludes that, within practical limits, the narrower the furnace-shaft is constructed the more energetic the actions of reduction and carbon-impregnation will be. This view is supported by the outlines of the ten furnaces shown in Fig. 59. It may be noted that the Union No. 2 (6 in table) and the Treibach No. 3 (8 in table) do not owe their low fuel consumption to great capacity, to the employment of high temperature of blast, nor to the great length of time the materials are allowed to remain in the furnace.

It was formerly the practice to allow the waste gases to burn at the throat of the furnace. Since the introduction of the hot blast, however, it has become usual to apply some arrangement for closing the throat of the furnace and for collecting the waste gas. The *cup and cone*, invented by Parry, is the arrangement generally used. The throat is closed by an iron cup-shaped casting, the diameter of which at the lower end is about one-half of that of the throat of the furnace. Beneath this cup, a cast-iron cone is suspended from its apex, and when the charge has descended

* *Engineering*, vol. xlii. (1886), p. 513; *Trans. Amer. Inst. Min. E.* vol. xv., 1887, p. 419.

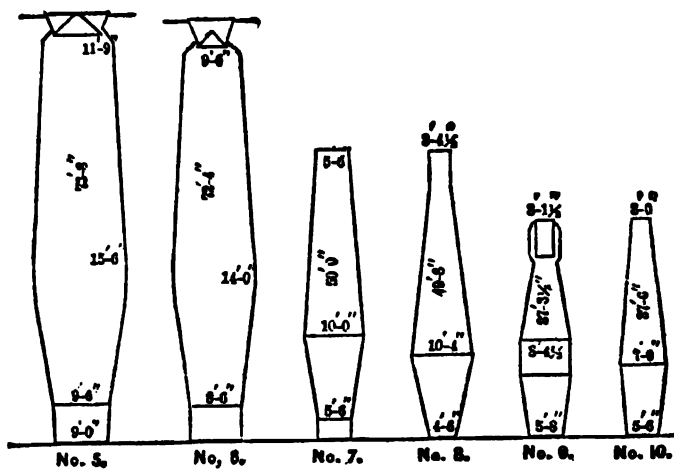
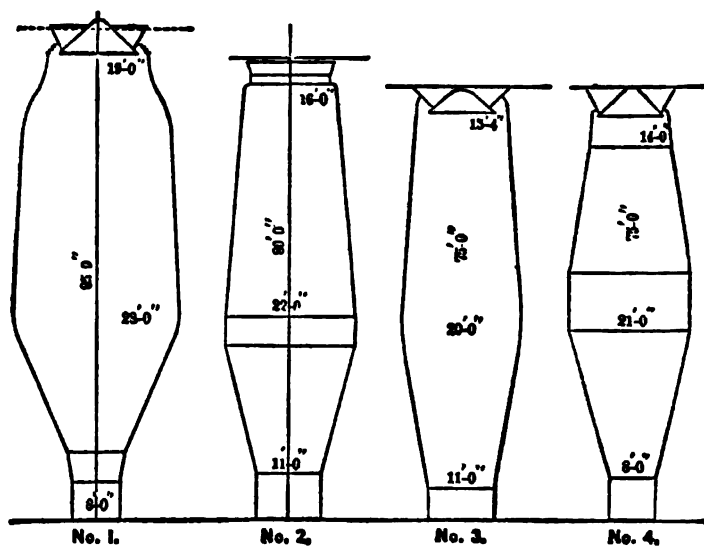


FIG. 59.

from the cup which forms a hopper, the cone is raised so as to completely close the throat, and the gases pass out through a lateral pipe: This method of closing the top is shown in Fig. 6o, where the effect of varying the size of the cup and cone is also indicated.

In Germany, arrangements are largely used by means of which the gases are withdrawn from the centre of the throat instead of from the sides. The apparatus of Langen and of Von Hoff afford good examples. In the former, the bell-shaped tube which

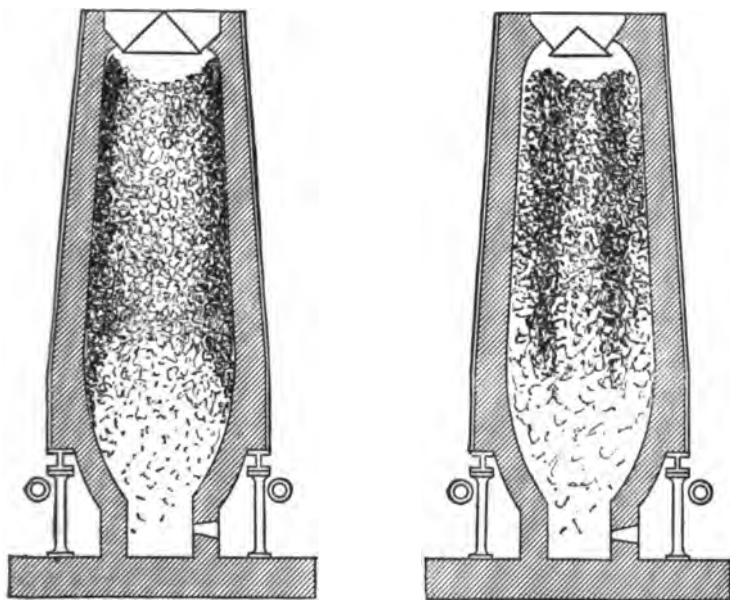


FIG. 6o.

closes the throat is raised, whilst in the latter it is lowered, in order to allow the charge to fall into the furnace. In both cases, gas-tight joints are obtained by the aid of water troughs.

Numerous attempts have been made to ascertain the changes in the materials during their descent in a blast-furnace, with reference to the arrangement of the constituents. A valuable series of experiments have been made by Profs. R. H. Richards and R. W.

Lodge* with a view to elucidate this subject. They constructed a model consisting of a vertical section of a furnace at the Edgar Thomson works (Fig. 6c), 40 in. in height, and made to the scale of half an inch to the foot. The horizontal section of the space through which the charge falling at any point in the descent is $1\frac{1}{2}$ inch multiplied by the diameter of the furnace at that place. The back and sides of the model were of wood, and the front of glass, the intermediate space measuring $1\frac{1}{2}$ inch. Below was a small hopper into which the charge fell, and from which it was shovelled back to the cup and cone. Every shovelful withdrawn settled the contents of the stack sufficiently to receive a new charge above, and in this way a great variety of feeds were tried, and the arrangement caused by them observed through the glass. The material used for the charges was composed of pebbles and clean quartz sand, the different sizes being mixed in the following proportions per cent. :—

	Lot 1.	Lot 2.	Lot 3.	Lot 4.
Through $\frac{1}{2}$ in. sieve on $\frac{1}{4}$ in. sieve .	38.74	51.66	64.0	76.08
" $\frac{1}{4}$ in. " $\frac{1}{8}$ in. " .	2.56	1.81	2.0	2.43
" $\frac{1}{8}$ in. " $\frac{1}{16}$ in. " .	13.67	11.17	9.0	6.39
" $\frac{1}{16}$ in. " $\frac{1}{32}$ in. " .	4.56	3.32	2.3	1.40
" $\frac{1}{32}$ in. sieve	40.46	32.02	22.7	13.69

Each lot of materials so mixed was used for a series of tests, and in every case, as soon as the model had got into normal working, a photograph of the condition of the charge was taken. These photographs are in series, with two variables, namely, the kind of cone or distributor, and the proportion of coarse and fine in the material used. A similar model may be seen in the author's lecture-room, where it has been found very useful.

An examination of the photographs shows:—1. That a cone which is large in reference to the stock line, always gives the charge in three columns, the two outer being fine and the one inner being coarse. 2. That a cone which is small in reference to the stock line and which is kept full fed, always yields the charge in five columns; the centre is coarse, then a ring of fine, and then margins of coarse again. 3. That a furnace fed without a cone, and whose top is smaller than the stock line, will give a fairly even mixture, the coarse material being slightly concen-

* *Transactions of the American Institute of Mining Engineers*, vol. xvi. (1888), p. 149.

trated in the margin. 4. That a furnace fed with a central funnel gives three columns, one fine in the centre and two coarse columns on the sides. 5. That if the stock line be varied from high to low, with a small cone, the arrangement of material resulting will vary from five to three columns. 6. Columns of coarse material appear to settle more rapidly, and those of fine material less rapidly.

With a view to produce a better distribution of heat, Truran proposed, in 1857, to increase the sectional area of the blast-furnace from the hearth to the throat. This plan was adopted by Raschette in 1862. His furnace in section is a narrow rectangle with six or eight tuyeres on each side, placed so as not to be directly opposite. Under the hearth, there is a chamber containing a grate, communicating with channels traversing the masonry of the stack. The masonry may by this means be dried, and the construction of the furnace is not dependent on the season of the year. As the blast is distributed over a large section in the zone of fusion, the combustion in this furnace is perfect, and a large out-turn is possible. The Raschette furnace is used in the Ural for smelting iron ores, but it has not been found to answer for this purpose in other parts of Europe. It is, however, largely used for smelting lead and copper ores. The Raschette furnace used for smelting lead ores in the Upper Hartz is 20 feet high, 7 feet 6 inches long, 4 feet 10 inches wide at top, and 3 feet at bottom. There are five tuyeres at each side, and, in the more recent furnace, one at each end.

Rectangular furnaces of the Raschette type are largely used in Colorado for lead-smelting. The furnaces used at Leadville are described in great detail by Mr. S. F. Emmons.* The furnace is formed of two independent parts, the masonry stack, *a*, (Figs. 61, 62) supported on a main cast-iron plate, *b*, resting on cast-iron pillars, *c*, and the crucible upon which rest the water jackets. These constitute one of the greatest improvements ever introduced in the construction of blast-furnaces. They are hollow boxes, made of cast-iron, malleable iron, or steel boiler-plate, in which water circulates freely, so that the temperature of this portion of the furnace wall, where the most intense heat prevails in the interior, never exceeds 70°. The water-jacket arrangement is always sectional, so as to afford every facility for the removal of the jackets when the furnaces need important repairs. This arrangement must be highly commended, as it

* *Geology and Mining Industry of Leadville, Colorado*, Washington, 1886, p. 659. See also papers to which reference is given on page 339.

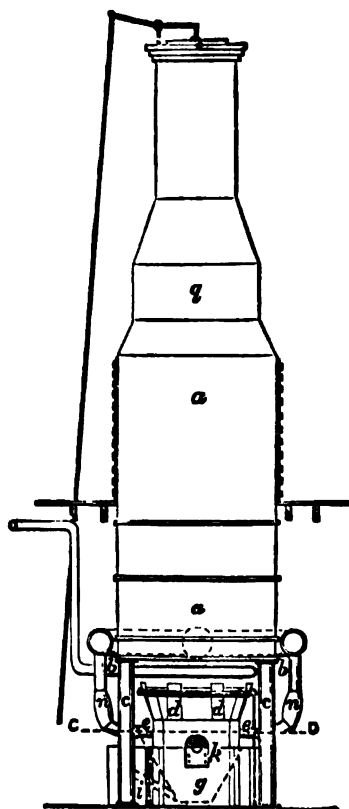


FIG. 61.

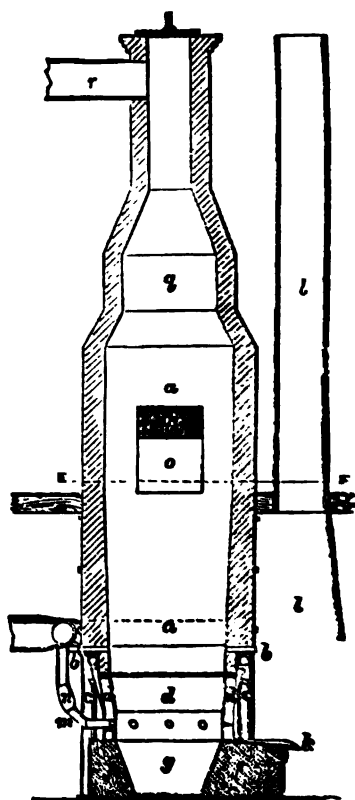
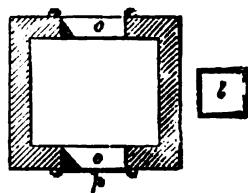
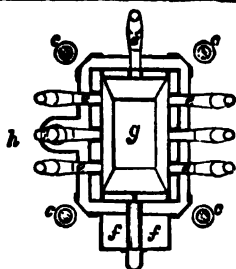


FIG. 62.



admits of the expansion and contraction of this portion of the furnace without altering the relative positions of the parts. The importance of this arrangement will be appreciated when it is stated that smelting campaigns of thirteen months are known at Leadville.

The Leadville rectangular furnace is shown in the accompanying figures, 61 and 62, which are drawn to a scale of 9 feet to the inch. The dimensions of the furnaces vary at the different works, as the daily smelting capacity varies from 15 to 40 tons. The water-jackets, *d*, are, in the furnace represented, twelve in number, bolted together and provided with openings for the tuyeres, *e*. A cold-water pipe runs round the furnace, and supplies water to the water-jackets. The lower ends of the latter rest on the hearth, *f*, which consists of cast-iron plates lined with fire-bricks

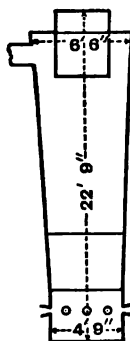


FIG. 63.

or brasque. The usual form of the bottom is shown at *g*. The hearth-plates enclose the leadwell, *h*, and the channel, *i*, through which the molten lead rises to the level that it occupies in the furnace, and can be ladled into moulds without interrupting the work. At the side of the furnace, an opening is left in the water-jacket for tapping off the slag, which runs down the gutter, *k*, when the clay stopping the aperture is pierced. A hood, *l*, is placed so as to carry off any fumes evolved during tapping. When cold blast is employed, the tuyeres are connected to the blast-pipes by flexible canvas hose, *n*, and a slide, *m*, at the elbow of the nozzle, admits of looking into the interior of the furnace.

The feed openings, *o*, are closed by counterpoised doors, *p*, and the furnace terminates in a short chimney, *q*, communicating by a flue, *r*, with dust-chambers.

Blast-furnaces of the Pilz type are also used in Colorado; but the rectangular furnace of the Raschette type is generally preferred, as it is less expensive in construction. In Europe, on the other hand, the former has almost entirely superseded the latter. The Pilz furnace, which is generally employed for smelting mixed ores of lead and copper, is circular in section. Its internal profile, which is shown in Fig. 63, differs from any of the types given in Fig. 59. In this case $\frac{H}{D}$ is more than three, but the widest part is at the top, the contraction being gradual to the "crucible" portion of the furnace in which the tuyeres are placed. The

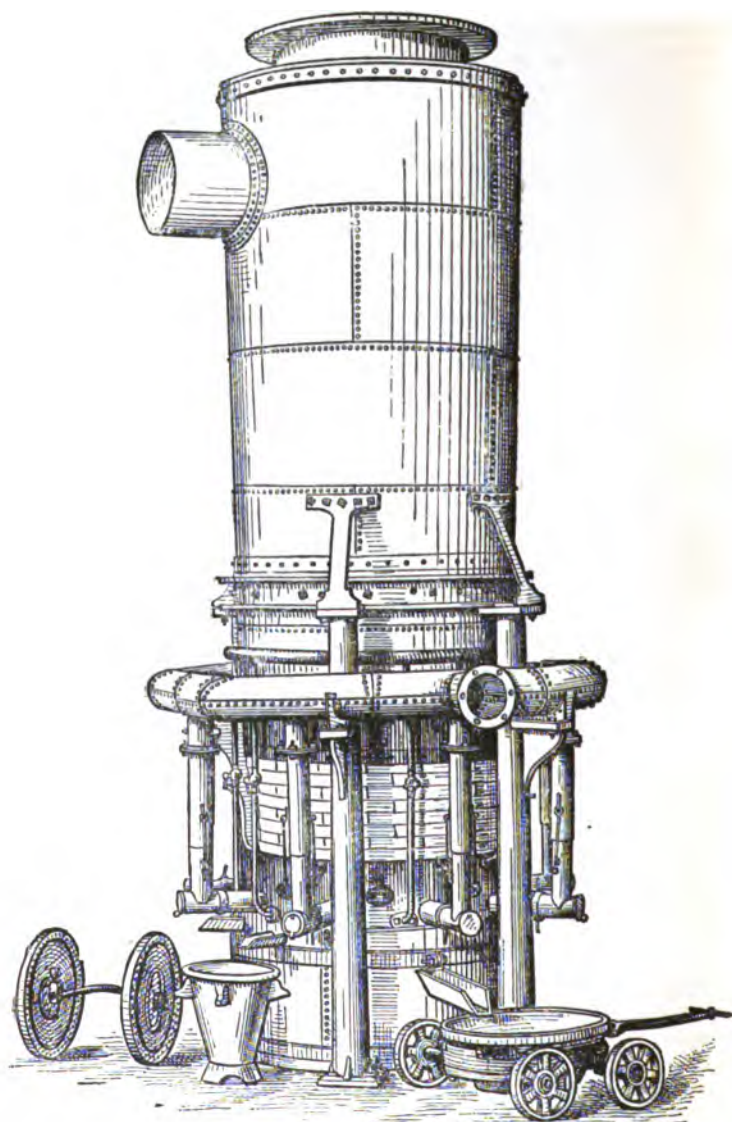


FIG. 64.

actual area at the throat is, however, much restricted by a cylinder of wrought iron through which the charge is introduced. The appearance of the exterior of the furnace, in its most recent form as used at Freiberg, is shown in Fig. 64.

3. **Reverberatory Furnaces.**—These are constructed of very varied forms and dimensions, but their construction is guided by principles common to them all. Reference to Figs. 65 and 66 will show that the reverberatory furnace consists of two main portions, the fire-place (either an ordinary grate or a producer), and the laboratory part, the fuel being separated from the ore, or the material to be heated, by means of a *fire-bridge*, which is simply a wall of refractory brick, usually furnished with an air-channel to keep it cool, and sometimes provided with orifices which admit air into the furnace. As the flames pass over this bridge and *reverberate*

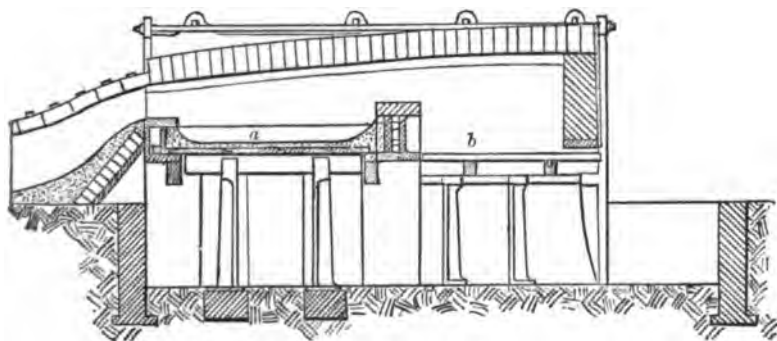


FIG. 65.

into the laboratory part, it will be evident that its height in relation to the position of the roof has to be regulated with much care, for on it will depend whether the flames act directly or by radiation on the material to be heated.

The laboratory part is connected, by means of a flue, with a chimney, which serves for the withdrawal of the consumed gases, and in many cases also for the production of draught. A damper at the base of the chimney or in the flue enables the current of air to be regulated; and, taken in connection with the thickness of the layer of fuel burnt on the fire-place, the atmosphere may be rendered oxidising, neutral or reducing at will. It is now necessary to consider the way in which the details and dimensions of the furnace may be varied. Figs. 65, 66, exhibiting

two extreme cases, show how much the dimensions of the laboratory part in relation to the fire-place may vary. In Fig. 66 a more or less pulverulent material has to be kept compara-

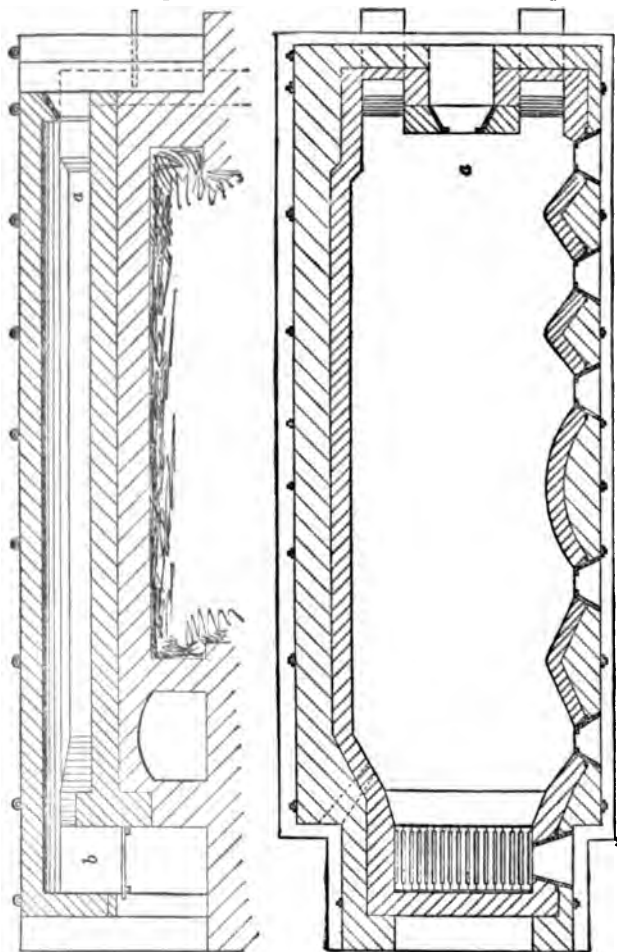


FIG. 66.

tively cool at the end of the furnace furthest from the fire-place, *b*, and to be gradually advanced to the hottest part, which is, of course, in close proximity to the fire-place. On the other hand,

in Fig. 65, a puddling furnace, the material, although energetically stirred, retains its original position on the bed, *a*, and has to be actually melted. In the former case the bed of the furnace is a plane, which may slope, but which is usually horizontal. In cases similar to the latter, in which the charge has to be wholly or partially melted, the bed is concave. The nature of the material of which the furnace-bed is composed is very varied. In cases where the temperature is not high, as in the calcination of lead ore, fire-bricks, which need not be very refractory, are used. In copper-smelting furnaces some 2 feet of siliceous sand is rammed tight. Brickwork is unsuitable for this purpose, as the regulus, or copper, resting on it works down through the joints. In Swansea the furnace bottoms are made of a moderately refractory sand containing 88 per cent. of silica. In certain lead-smelting furnaces the working bottom of the furnace is made of the grey slag supplied by the furnace itself. The bed of the puddling furnace introduced by Cort was made of sand. In 1818 the iron bottom was substituted with great advantage.

In order to show the way in which the dimensions of furnaces employed for different purposes are related, it will be well to give the following examples based on data furnished by Gruner:—

1. In a reverberatory furnace used at Swansea for the refining of copper, in which anthracite is burnt, the volume of the laboratory is 158 cubic feet, the sectional area of the fire-place is 19 square feet, the consumption of anthracite is 2.30 lbs. per square foot of fire-place per hour, the cubic contents of the laboratory is 8.3 cubic feet for every square foot of the fire-place, and the weight of the material treated is 10 tons. The temperature attained is high, as copper has to be melted; but it falls far short of that required in the puddling furnace where wrought iron has to be kept near its melting point.

2. In a puddling furnace it will be seen that the volume of the laboratory in relation to the sectional area of the fire-place is relatively much smaller. Thus, in a puddling furnace in operation in South Wales, the volume of the laboratory is 35 cubic feet, the sectional area of the fire-place is 9 square feet, the consumption of coal is 3.6 lbs. per square foot of fire-place per hour, the cubic contents of the laboratory is 3.9 cubic feet for every square foot of the fire-place, and the weight of the material treated

EXAMPLES OF REVERBERATORY FURNACES.

	1. German Long-bedded Calorner.	2. Copper-furnace for Argo Works Denver.	2a. Caldera (Chim) Copper-furnace (Kew).	3. Cwm Avon (S. Wales) Copper-furnace (Levy).	4. Butte Copper-furnace (Peters).	5. Flowing Lead-furnace.	6. Pintabre Lead-furnace.	7. South Staffordshire Riddling Furnace (Model in the School of Mines).	8. English Cupellation Furnace.
Length of hearth . . .	ft. in. 39 0	ft. in. 22 0	ft. in. 16 6	ft. in. 16 0	ft. in. 14 6	ft. in. 11 6	ft. in. 11 0	ft. in. 5 3	ft. in. 1 9
Width of hearth at middle . .	9 0	18 6	11 6	12 0	11 6	7 0	9 6	4 9	4 0
Length of fire-place . . .	6 6	4 0	5 8	4 0	4 6	2 6	2 6	3 9	2 0
Width of fire-place . . .	1 6	5 0	5 3	4 0	4 0	2 6	4 3	3 9	1 10
Depth of fire-place below top of bridge . . .	—	2 6	1 5	3 6	2 4	2 6	1 9	1 6	1 9
Height of bridge above hearth .	—	4 0	1 2	—	1 4	1 0	0 9	0 6	—
Height of chimney . . .	—	60 0	—	—	50 0	—	—	30-50 ft.	—

In the table on the preceding page the dimensions of typical reverberatory furnaces are given. No. 1 is a German furnace for roasting galena, a long-bedded calciner (*Fortschaufelungssofen*). There are four working doors; 15 cwt. of raw ore are charged in every six hours at the flue end of the furnace. The furnace is thus able to calcine 3 tons of ore in twenty-four hours. No. 2 and 2a are reverberatory furnaces for smelting copper. The same dimensions apply to the furnaces used for ore-smelting, for smelting for "blue metal," and for roasting-smelting for Chili bars. In the ore-smelting furnace, the length of the operation is seven and a half hours, the charge 3.52 tons, and the consumption of fuel 0.52 ton of bituminous coal.

No. 3 is the South Wales copper-furnace, the same dimensions applying to the furnaces for ore-smelting, for the smelting of the different kinds of regulus known as "blue metal," for white metal and for blister copper. No. 4 is an American furnace used for ore-smelting. The charge is 3.3 tons, and the duration of the operation five hours, the consumption of fuel amounting to 10 cwt. of bituminous coal. No. 5 is the so-called flowing furnace used for lead-smelting by the Cornish method. There are two doors on each side. The charge is 2 tons of calcined ore, which is spread over the sloping bed. It melts in about three hours. The charge is then mixed with lime and anthracite and 2 cwt. of scrap iron are placed in the furnace at the tap-hole. The charge is then re-melted, and the furnace tapped by means of an iron bar. The reduced lead flows into a pot outside the furnace, and is followed by regulus formed in the reduction of lead sulphide by iron in the second fusion. Finally, the slag begins to flow and runs along a gutter into a pit outside. The whole operation occupies eight hours, the consumption of coal being 9 cwt. per ton of ore. No. 6 is the Flintshire furnace used for lead-smelting. There are three doors on each side, the front ones being used for stirring the charge, and the back ones for tapping the slag. The roof is low and inclines towards the flue end. In the middle there is a hopper for charging. The bed slopes from all sides towards a well, in front of the tap-hole, where reduced lead collects. The usual charge is 21 cwt. of ore, the consumption of coal being 12 to 16 cwt. No. 7 (Fig. 65) is a South Staffordshire puddling furnace, which may be taken as typical of this class. There is a model of it at the School of Mines, London. The roof is a low, flat arch with a slight slope towards the flue end. The working door, placed at one side of the furnace, is about 10 inches above the furnace bottom. It is closed by a fire-brick slab, suspended from a lever. Below the door is the tap-hole, which is closed with sand

during the working of the furnace. No. 8 is the English cupellation-furnace, in which lead is separated from silver by the joint action of air and heat. The bed of this furnace is movable and is made of bone-ash, a material that resists the corroding action of the litharge (lead oxide) formed during the process. The movable bed, or *test*, consists of an oval wrought-iron frame lined with bone-ash. One end of the test is perforated with a number of holes through which the litharge, as it forms, flows into a receptacle below. A large portion of the litharge is, however, absorbed by the bed. Air is supplied by means of a tuyere. In the German cupellation-furnace, which is also of the reverberatory type, the roof is movable and the bed fixed. The latter is concave and circular, 8 to 10 feet in diameter; it is made of marl. The roof consists of a movable iron cover lined with clay. A pair of inclined tuyeres at one side of the bed supply the necessary air, and the litharge flows off through an opening on the opposite side.

The most important reverberatory furnace in which gaseous fuel is employed is the regenerative open-hearth steel-melting furnace of Sir W. Siemens. Steel is produced in this furnace by three methods: (1) by the fusion of a mixture of pig iron and scrap iron; (2) by the fusion of pig iron with rich oxides of iron; and (3) by a combination of these two processes (the Siemens-Martin process).

The regenerative furnace of Siemens is provided with a multiple series of passages in refractory bricks piled one over the other. These passages are traversed alternately by the burnt gases which give up their heat, and by the air or gas which enters to perform the work required in the metallurgical operation. By giving the conduit sufficient length and the hot gases a slight velocity they may be made to issue almost cold, whilst the air which it is proposed to heat gradually reaches hotter and hotter regions. The heating appliances vary in character according to whether the gas and air are at high or low pressure. When the tension is low, chambers or conduits in refractory brick will be sufficient; but when the tension is high, the entire system of heating appliance must be enveloped in a case of sheet-iron, in which air may be compressed.

The usual form of regenerative furnace resembles an ordinary reverberatory furnace symmetrically arranged at its two ends instead of having the grate at one end and the flue at the other. Chambers near this are filled with brick so piled that air or gas can freely circulate. The combustible gas enters by a tunnel into one of these chambers, and the air to effect the combustion enters

by another tunnel into another chamber. The gas and air are both led to the hearth, where they meet, and the air burning the gas, the flame produced plays freely on the material on the hearth. The burnt gases then pass into two other chambers, and in slowly passing through them give up their heat to the bricks and finally reach the chimney. In the direct passage which the gases traverse there are two valves, by means of which the direction of the current may readily be reversed. When the bricks have acquired a temperature but little lower than that of the burnt gas, the valves are turned through an angle of 90° . The combustible gases then enter one of the chambers just heated, and the air enters the other, and in slowly ascending through the chambers they become heated at the expense of the bricks; they meet at the hearth as before, and in burning develop a degree of heat, the intensity of which depends on the extent to which they have been heated. The products of combustion, after having done their work on the hearth of the furnace, pass through the chambers first mentioned to the chimney. When these chambers become heated, the direction of the current is again reversed, and so on.

By this alternate play of the valves the air and the combustible gas are heated; the temperature of combustion is thus increased, and a very high temperature may be obtained. At the same time, even if the temperature that would be obtained without this preliminary heating were sufficient for the required operation, it is obvious that by heating the air and combustible gas, a great economy in fuel can be effected.

In order to ensure that the gas shall not escape into the chimney at a temperature higher than 100° to 150° , it is necessary for there to be 14 or 15 sq. ft. of brick surface for every 2 lbs. of coal burnt between two reversals. The arrangement of the bricks in the chambers is not a matter of indifference. They should be so disposed as to leave as much space free as full. At the base, however, the passage should be restricted in order to force the gas to pass in a more uniform manner through the mass. The drying, the lighting, and the reversal of the valves must be effected with precaution. It is necessary to avoid explosive mixtures of air and gas. This is easily effected by diminishing the supply of air.

The great advantage of the regenerative furnace is that an oxidising, neutral, or reducing atmosphere may be obtained at will by regulating the supply of air.

The gas, it will be noted, does not come from any fire-place in the furnace itself, but is generated in a separate appliance. This

gas-producer consists essentially of a fire-grate on which a thick layer of fuel is maintained. The combustible part of the coal, usually small coal, is converted into carbonic oxide, hydrogen, and hydrocarbons, which are carried forward through flues to the furnaces in which they are burnt.

The gases on leaving the producer have an initial temperature of about 350° . By a curious syphon-like arrangement, they are made to rush forward with increased velocity. They are cooled in the vertical part of a tube, and then, as their density is thus increased, they rush down the tube with increased velocity.

Mr. F. Siemens has modified the original open-hearth furnace by substituting a domed roof for the flattened one previously used. The ports in this furnace are horizontal, and consequently the gas burns in an enlarged chamber above the bed out of contact with the roof or the charge. The work is thus done by radiation, by which means the durability of the furnace has been much increased.

In a new form of Siemens furnace, described by Mr. J. Head* and Mr. P. Pouff, the gases leaving the furnace-chamber are directed, partly through an air regenerator and partly under the grate of the producer, there to be reconverted into combustible gases, and to do the work of distilling hydrocarbons from the coal. In fact, the gas-producer in this case utilises the heat formerly deposited in the gas-regenerators, and in doing so transforms spent gases into combustible gases. For the propulsion of the gases through the converter-producer, a steam jet is employed. The steam is superheated by the waste gases from the furnace, and mixing with them forms a very hot blast under the grate. This form of furnace may be constructed in various ways, the one shown in Fig. 67 having been successfully used in heating and welding iron. It is a radiation-furnace, heated by means of a horse-shoe flame. This form of flame offers advantages, but its adoption is not obligatory, as the flame may be made to traverse the heating chamber from end to end in the usual manner. A, A', are reversible regenerators for air, on the top of which is built the gas-producer or converter B, of which F, F', are the charging hoppers and N, N', the grates. The heating-chamber E, adjoins the producer resting on the ground, or in some cases a pit may be provided below it. C, C', are the flues leading the combustible gas to the furnace chamber E, the passage of the gas in these flues being controlled by the valves D, D', at the two ends of a rocking-beam, so that the outlets are opened and shut

* *Journ. Iron and Steel Inst.*, 1889, No. ii. p. 256.

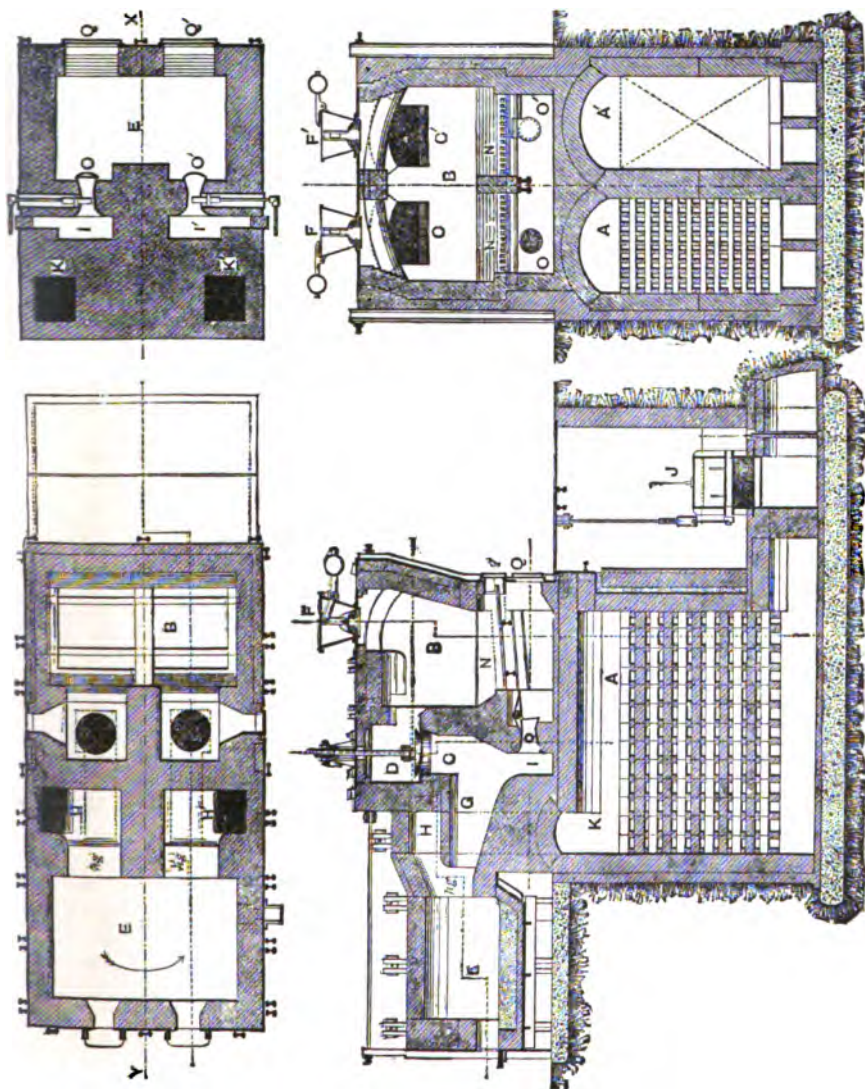


FIG. 67.

alternately to convey the gas to one or other of two ports (one shown) G, of the heating-chamber E. H, H', are the air-ports of the heating-chamber, communicating through the flues K, K', with the regenerators A, A'. I, I', are steam-jets, placed in the return flues, for directing a portion of the waste products of combustion to the grates of the converter. J is the valve for reversing the direction of the air flowing into the furnace, and of the products of combustion through the regenerators to the chimney-flue. O, O', are hinged caps for alternately admitting and shutting off the products of combustion from the heating-chamber to the converter. These caps are worked automatically by means of the connections O, O', attached to the rocking-beam, the same movement which closes D opening O', and that which closes D' opening O. Q, q, are doors for giving access to the grates of the converter for clearing them.

The mode of working the furnace is as follows:—Gas from the converter B passes through the flue C' and the valve D' to the gas-port G', and into the combustion-chamber h' g'. Air for combustion passes through the regenerator A', the air-flue K', and the air-port H' into the combustion-chamber, where it meets the gas from the converter, and combustion ensues. The horse-shoe flame sweeps round the heating-chamber E, the products of combustion passing away by the second combustion-chamber h g, go partly through the regenerator A, and reversing valve J into the chimney-flue, and partly down the flue G, whence they are drawn by means of the steam jet I through the capped inlet O under the grates of the producer B, there to be converted into combustible gases. From time to time the direction of the flame in the furnace is reversed by manipulating the rocking-beam, carrying the valves D, D', and the reversing valve J in the usual manner of working regenerative gas-furnaces. An auxiliary steam-jet is provided for supplying air to start the producer when the furnace is first heated up.

Besides the advantages in the saving of fuel, labour, and metal, the simplicity of design of the new furnace renders its cost of construction not much greater than that of a solid-fuel furnace, while its cost of maintenance is very much less. The cost of construction of the new furnace is found to be about two-fifths of that of the old form of regenerative gas-furnace, of the same productive capacity, with separate gas-producers and gas-regenerators, and the space occupied below ground is also considerably reduced.

In order to economise labour, various modifications of the reverberatory furnace have been invented. The laboratory has been

considerably increased in height, and the material allowed to fall as a shower of dust through a shaft that is traversed from bottom to top by the flame from a lateral fire-place. In some cases the dust falls freely; in others there are obstacles in the way. The most successful furnace of the former class is that

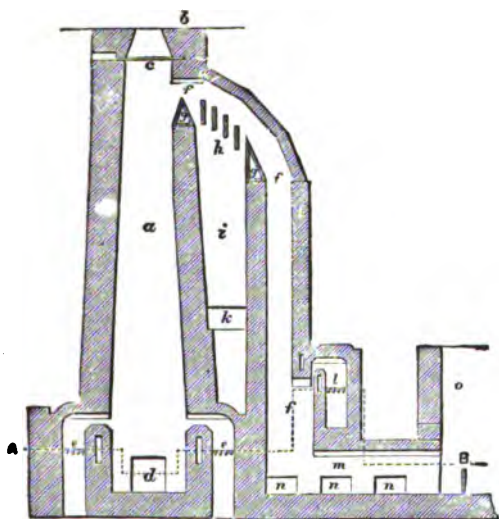


FIG. 68.

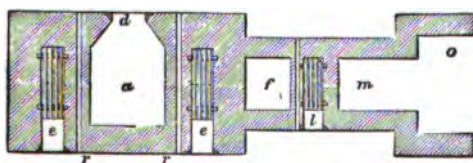


FIG. 69.

of Stetefeldt for roasting argentiferous ores. The furnaces of Gerstenhöfer and Hasenclever may be taken as types of the latter class.

In the Stetefeldt furnace, the pulverised ore, mixed with salt, is charged in at the top of the shaft *a* (Figs. 68 and 69) by the aid of a mechanical feeder arranged at *b* on the top of the shaft. The ore falls in a slow stream down the shaft and encounters the hot gases from the fire-places, *e*, *e*. For the ore which is carried

along the flue, *f*, through which the gases escape, a third fire-place, *l*, is provided. This assists the action of the main shaft, and causes the ore to reach the flue *m* in a completely roasted and chloridised state, if it has not already been discharged through the door *d* upon the cooling floor. At *h* there are cast-iron plates, which form the bottom of the flue, and which allow any dust settling to fall into the chamber *i*, whence it is removed through the door *k*. The flue bridges, *g, g*, are of cast-iron. The fire-places and arches are of fire-brick; the remainder of the furnace is of common brick. The vertical shaft is usually 30 to 35 feet in height, and 4 to 5 feet square at the base. These furnaces roast about 40 tons of ore in twenty-four hours. In Utah as much as 64 tons are treated daily. In the Stetefeldt furnace the chloridising roasting action is very rapid and complete, whilst the expenditure of labour and of fuel is small.*

The Brückner cylinder (Fig. 69a) is another and successful modification of the reverberatory furnace designed with a special view to the economy of labour. The roasting chamber or laboratory part of the furnace consists of a horizontal iron cylinder *O*, about 8 feet in diameter, which may be lined with fire-brick. The ore is introduced into this cylinder in the state of coarse powder from an ore bin *B*, through two doors *D D* in the side of the cylinder, the latter being first rotated so as to bring the doors vertically beneath the two hoppers of the bin. The openings are closed by slides, by means of which the supply of ore to the cylinder can be controlled.

When the charge for the operation is received in the cylinder the two doors *D D* are closed and bolted down, and the cylinder, which rests upon large friction rollers *R R*, is slowly revolved by means of the gearing *G G*, so that fresh surfaces of the ore are continually exposed to the action of the heated gases from a hearth *F*. This hearth is mounted upon wheels and stands upon a short length of rails, so that when desired it can be brought away from the end of the cylinder and leave the latter open for examination and repair. The gaseous products pass out of the cylinder into a dust chamber *H*, constructed in brickwork, and thence are discharged into suitable flues.

When the roasting is completed, the cylinder is stopped with its doors *D D* immediately over two trucks *T T*, which are placed so as to receive the hot roasted material as it is raked through the doors. Lateral movement of the cylinder is prevented by the rollers *K K*, which are placed so as to bear upon either side of one of the

* *Engineering*. vol. xl, 1885, Sept. 25., p. 293.

rings L L, which also serve to support the cylinder upon the friction rollers.

Another form of reverberatory furnace for the roasting of ores, known as the O'Hara furnace, is much used in America. It resembles the ordinary roaster, but has in addition an endless chain mounted upon rollers and provided with a series of plough-shaped scrapers. The chain is kept in motion by means of suitable gearing, so that the scrapers are continually exposing fresh surfaces of ore to the action of the heated current of gases.

4. **Closed-vessel Furnaces.**—In furnaces of this class the material to be heated is separated from the fuel by an envelope, in the form of a closed vessel. The vessel is heated by being in contact with the fuel, or by the flame developed from a fire on a grate, or lastly by the gases from a producer. The form of the vessel is determined by the process that is to be undertaken.

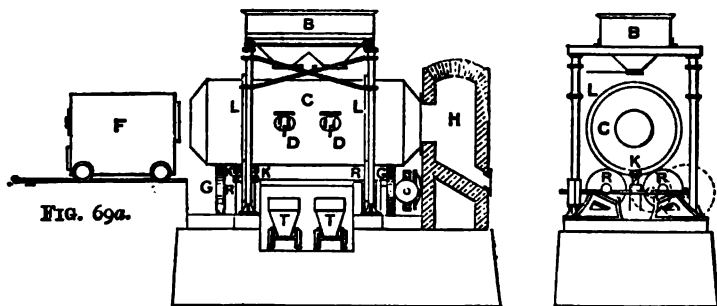


FIG. 69a.

Thus, for simple heating, the muffle is employed, whilst for fusion crucibles are used. Retorts and similar vessels are used exclusively for distillation and sublimation.

The ordinary assay furnace may be taken as typical of the wind-furnaces used by the brass-founder. These furnaces vary according to the size and number of crucibles inserted in them. The crucible gas-furnace used for melting steel consists of a long hearth on which the crucibles are placed in pairs. This hearth has a movable roof through which the crucibles may be withdrawn, and on the long sides are the flues from the regenerators, the construction of which is similar to that of other regenerative furnaces.

The best example of a retort-furnace is afforded by the furnace used in Belgium for smelting zinc ores. In this furnace the ores are reduced in a number of fire-clay retorts with a bellied fire-clay nozzle in which the zinc condenses, and a sheet-iron tube in which

the zinc oxide is collected. The retorts are placed in rows in a vertical arched chamber, with a fire-place at the base. In recent furnaces of this kind the fire-place is arranged for gaseous firing.

The furnaces are usually built in pairs, back to back. At Angleur* they contain 160 retorts on either side. The charge for each retort is 25 lbs. of a mixture of equal weights of powdered roasted blende and non-caking coal.

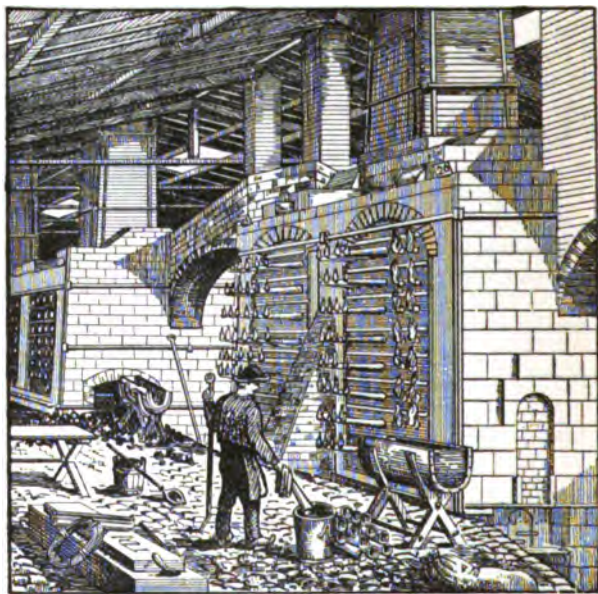


FIG. 70.

An external view of the Belgian zinc furnace is shown in Fig. 70.

Retort-furnaces are also used for smelting mercury ores, the condensers sometimes consisting of earthen pipes, or *aludels* (Fig. 71), thrust one into another. The ore is roasted in a circular kiln with a system of openings connecting with a series of ranges of aludels resting on the doubly inclined surface of a

* See article Zinc, by de Lalande, in Wurtz, *Dict. de Chem.*, p. 754.

terrace. In the recent furnaces at Almadén there are sixteen of these ranges.*



FIG. 71.

The tube-furnace is occasionally employed in the extraction of bismuth from its ores by liquation. Native bismuth melts at 264° , and advantage was taken of this fact to separate it from the more or less infusible materials accompanying it. This process has, however, been almost entirely supplanted by ordinary smelting and wet methods. The liquation-furnace, used at Schneeberg, in Saxony, contains a series of cast-iron tubes, oval in section, and inclining towards the front, where the ore is placed. The liquated metal is received in iron vessels heated by a separate fire.

A furnace of the closed-vessel type is used in the manufacture of steel by the addition of carbon to malleable iron, a process termed *cementation*. The furnace (Fig. 72) consists of a rectangular chamber supplied with chimneys, *c c*, and divided into two parts by a fire-place, *a*, on either side of which is a rectangular fire-brick vessel, or *converting-pot*, *b*, varying from 8 to 15 feet in length and 3 feet in width and depth. These pots are thoroughly heated by the flames, and the products of combustion reach the conical hood, *e*, some 40 feet in height, which serves to prevent loss of heat by radiation as well as to carry off the smoke. At *d* there is a man-hole, built up during the working of the furnace, but opened for cooling down and for the withdrawal of the charge.

The Bessemer Converter.—This furnace has the shape of a pear, the form originally given it by Bessemer. Unlike all other smelting furnaces, the converter is usually not fixed but supported on standards by trunnions. To one of these a pinion is keyed, by means of which the vessel can be moved through an angle of 170° , so that the molten metal may be poured from its mouth. The other trunnion is hollow and admits the blast to the vessel. A pipe from this trunnion passes to the tuyere-box, forming the bottom of the converter, which is perforated by ten to nineteen circular holes, into each of which is placed a conical fire-clay tuyere, perforated with twelve holes each $\frac{3}{8}$ inch in diameter.

* *Revista Minera*, 1889, p. 129.

The Bessemer process was first patented on October 17, 1855, and was described in a paper read before the British Association, in which the inventor claimed a method of making wrought-iron without using fuel, but it must be remembered that the combustion of the carbon, silicon,

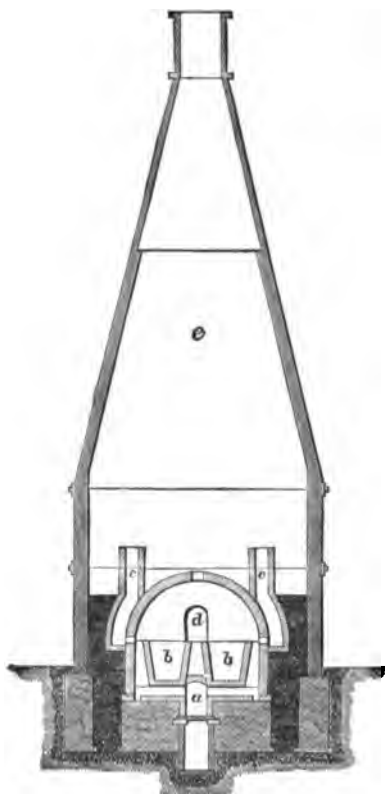


FIG. 72.

and other elements in the pig-iron during their elimination provides the heat necessary for maintaining even molten wrought-iron in a fluid state. The process consists essentially in blowing large quantities of compressed air through numerous small jets into a molten mass of pig-iron, thereby effecting the rapid combustion of the carbon, silicon and manganese present in the metal. The excitement caused by the invention in all iron-making countries was immense, as it was thought that the wrought-iron industry was doomed, since the quantity of pig-iron (about 3 tons) that a puddling furnace could treat in twenty-four hours, could be dealt with in the Bessemer converter in twenty minutes. It was, however, soon found that the expectations were not completely fulfilled; good steel could not be obtained from all kinds of pig-iron, as all the impurities could not be removed. Phosphorus, of which 1 to 2 thousandths suffice to render steel brittle

and cold-short, remained completely unattacked. It was, therefore, necessary to employ pure pig-iron containing but a low proportion of phosphorus. Previous to 1855, the annual production of steel in Great Britain was 51,000 tons, at a price of about £50 per ton. At the present time, in Sheffield alone, 830,000

tons are produced annually, and throughout Europe 3,000,000 tons, at a price of £4 to £10 per ton.

Bessemer's original rotating converter was spherical,* so as to reduce the loss of heat by radiation as far as possible. Some of his early experiments were made in an upright fixed cylindrical vessel, very similar to the Bessemer converters recently introduced for treating small charges.

The charge of pig-iron is either melted in a cupola or run directly from the blast-furnace into the converter. The blast is turned on, and combustion goes on in two stages:—

1. *Scorification*, during which stage the graphitic carbon passes into the combined state, silicon becomes oxidised, and silicates of iron and manganese are formed. This stage lasts from four to six minutes.

2. *Ebullition*, during which stage the carbon is rapidly oxidised by the blast, carbonic oxide being evolved in large quantities. This stage lasts six to eight minutes.

The first stage is accompanied by a reddish-yellow flame, the second by a more brilliant display of flame and sparks, and numerous small detonations. The first stage yields but little flame, as the products are solid—oxides of silicon and manganese. The products of the second stage, however, being gaseous—oxides of carbon—that stage is accompanied by a greater evolution of flame. As soon as the carbon has gone, the flame drops. A trained eye notices this immediately, and the operation must be stopped, or iron will be oxidised. It is usual to eliminate all the carbon, and then to add the required amount in the form of spiegeleisen. The manganese in the spiegeleisen is also useful—indeed, essential. It probably acts on dissolved oxides in the metal, and “masks” the action of the sulphur. When manganese only is required, ferro-manganese is added. This contains considerably more manganese than spiegeleisen does in proportion to its carbon.

The duration of a “blow” varies with the variety of pig-iron, its quantity, and the pressure of blast used. When the iron contains little silicon and manganese, the duration may be fifteen to twenty minutes; when the iron contains much of these elements, thirty minutes may be required. The loss of iron rarely exceeds 9 to 12 per cent. when the pig-iron is run direct, but it may reach 15 per cent. when the metal is remelted in a cupola. With a pair of converters working in conjunction, ten to fifteen blows per

* Sir H. Bessemer gives sixteen drawings of early forms of converters, *Journ. Iron and Steel Inst.*, 1886, p. 638.

twenty-four hours may be obtained, and when movable bottoms are applied to the converters, as many as twenty can be obtained in that time.

The details of the construction of the Bessemer converter may be seen from Fig. 73, which is from a drawing specially prepared for this work by Mr. P. O. Gilchrist. It represents the best form of converter for the basic Bessemer process.

The phosphorus is not eliminated in the "acid process," because the converter lining consists almost exclusively of silica and the oxides of phosphorus have a weaker acid reaction than the silica has. A basic slag is absolutely indispensable for the removal of the phosphorus, and even if the slag was not rich in silica derived from the silicon in the pig-iron, it could never acquire a basic character, since silica would be obtained from the lining. In 1835 Berthier showed that in the puddling process, the phosphorus was removed by the aid of basic slag (tap cinder), and attempts were made by von Tunner and by Gruner to replace the acid lining of the Bessemer converter by a basic one, so as to eliminate the phosphorus, but difficulties of various kinds presented themselves, until three School of Mines men, Snelus, Thomas, and Gilchrist, directed their attention to the problem. Dolomite, a mixture of calcium and magnesium carbonates, is calcined at a high temperature, then powdered, and mixed with heated anhydrous tar, and moulded into bricks under a pressure amounting to 200 atmospheres. The bottom of the converter is rammed out of the same material, and heated to incipient redness, whereby the greater portion of the tar is expelled. In a converter lined with this material, if lime be added to the charge, a basic slag may be produced, which combines with the phosphorus burnt to phosphoric anhydride.

If a pig-iron is selected for the basic Bessemer process containing as much silicon as that employed in the acid process, a large addition of lime is necessary, and so much slag is produced as to render the process almost impracticable. It is therefore found advisable to employ a white pig-iron containing a small percentage of silicon. In this case, although cold at first, the blow is very hot at the end, owing to the oxidation of the phosphorus. In this process it is necessary to melt the pig-iron in a cupola at a high temperature, to add hot lime, and to have large tuyeres and considerable pressure of blast.

The most suitable pig-iron for the basic Bessemer process contains—

Silicon.	Sulphur.	Phosphorus.	Manganese.	Carbon.
0.5 to 1.8 ...	under 0.3 ...	0.8 to 3.0 ...	under 2.5 ...	about 3.0

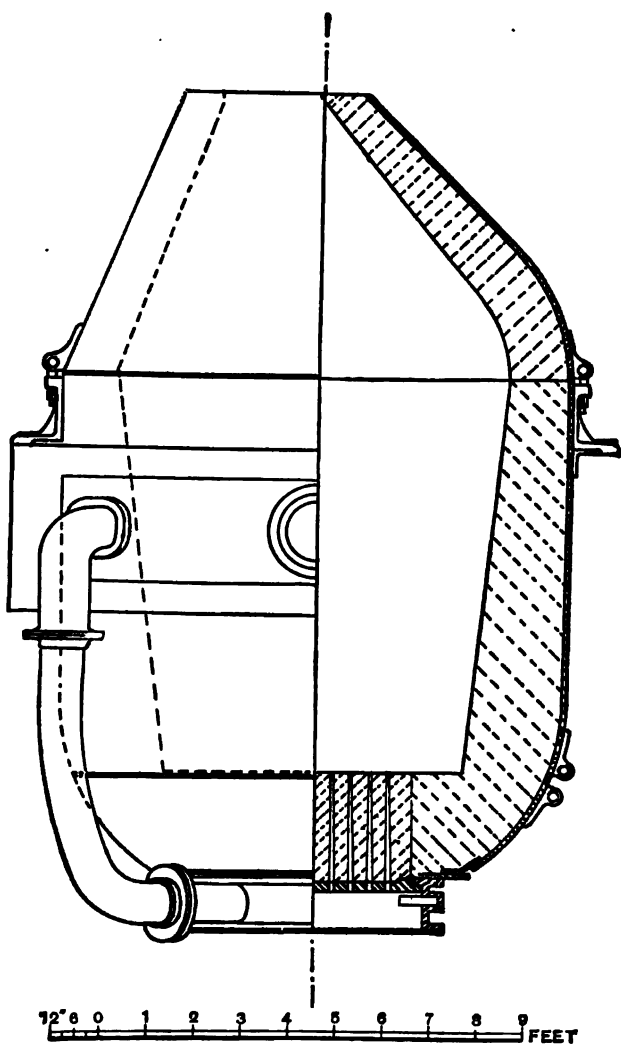


FIG. 73.

As the amount of sulphur is not sensibly reduced, 0.3 per cent. is the limit which may be present in the pig-iron.

One important feature of the basic process is the value of the slag incidentally produced. It consists chiefly of lime and phosphoric anhydride. Of the latter there is as much as 13 to 20 per cent. Both these materials are used as fertilisers by the agriculturist, and basic slag, as might have been expected, has been found to be a valuable manure. According to Gilchrist,* in 1889 as much as 600,000 tons of this slag were made, containing 17 per cent. of phosphoric anhydride and 60 per cent. of lime. It is, of course, not a suitable fertiliser for all soils, calcareous ones for instance, but for sour, peaty, and clay soils it is of great value, as is shown by the fact that all the 600,000 tons were sold at from 20s. to 30s. per ton at the works. It is interesting to note that the phosphoric anhydride is combined with the lime in an unusual manner. Instead of being an insoluble tribasic phosphate, it is a readily soluble tetra-basic phosphate, and, if it be finely ground, the phosphorus it contains is readily assimilated by plants. At first attempts were made to treat it by various chemical methods, but it has been found best to simply grind it and use it in fine powder.

Of late years an attempt has been made to revert to a type of converter employed by Sir Henry Bessemer in his earlier experiments. It is of small size and has horizontal tuyeres. In the case of the Clapp-Griffiths converter † these are symmetrically arranged in the walls of the converter near the base. There is a very low pressure of blast, 5 to 6 lbs. per square inch, and the valves are adjusted automatically. The converters are adapted to charges varying from 1 to 3 tons. The Robert converter ‡ is small, and is adapted to charges of 1 ton or more, the charges in no case exceeding 3 tons. By the action of the blast through a range of tuyeres inclined at different angles, a rotary motion is gradually imparted to the fluid metal. These tuyeres are placed high up in the converter, and by tilting it and by manipulating the blast-valve, the operator can change the volume and pressure of the blast. The converters are mounted on trunnions in the usual way, and are revolved by means of hand-gearing. The main point about these little appliances is that they bring the production of soft steel within the reach of small manufacturers. In Clapp-Griffiths' practice it has been found that by

* *Journ. Iron and Steel Inst.*, 1887, No. i. p. 212, where there is also a bibliography of the subject.

† *Ibid.*, 1883, No. ii. p. 705.

‡ F. L. Garrison, *Ibid.*, 1889, No. ii. p. 266.

keeping the carbon low, a certain amount of phosphorus may be allowed to remain in the steel without injury to the properties of the metal.

The Bessemer converter has been modified and employed for smelting copper regulus. The early experiments were not successful. In 1880, however, Pierre Manhès, the proprietor of the Vedènes copper works, Department of Vaucluse, France, obtained patents for its use in copper smelting, and smelting works were erected at Eguilles, near Avignon.*

The saving in fuel effected by the use of the converter is very considerable, and it is claimed that the Manhès process renders copper smelting possible in countries where, owing to the high price of fuel, the Welsh process is out of the question. As will subsequently be shown, the Welsh process consists of six to eight successive roastings and fusions in order to obtain coarse copper from the ore, all the operations being effected in large reverberatory furnaces. In the Manhès process from one to three of these operations are effected by blowing air through copper regulus in a converter which differs considerably from that employed for iron-smelting.

Its later form is a horizontal cylinder, holding about 1 ton of regulus, and turning on axial trunnions, through one of which the blast passes to a row of tuyeres, parallel to the axis. The level of the tuyeres can be altered as the "blow" progresses, and the copper as it is reduced sinks to the bottom of the converter, which is gradually turned so as to permit the blast to pass into the regulus above the level of the copper, which thus escapes chilling. The blow lasts 15 to 20 minutes, and at one operation "blister copper" may be obtained from the "white metal" of the Welsh smelter. For poorer regulus of 50 to 60 per cent. of copper (blue metal), it is well to blow twice in separate converters. The regulus may be run into the converter direct from the smelting furnace.

The electrical furnace, originally devised by Sir W. Siemens, will probably become a powerful instrument of research in the near future.

It consists, in one of its latest forms, shown in Fig. 73a, of a metallic framing K, lined with a non-conducting refractory material B, such as magnesia, and containing a crucible C R, that may be of carbon or other material. The framing has two metal castings M M mounted upon it, each of which carries a terminal A, and a carbon-holder V, placed at an angle of 45°

* *Annales des Mines*, 8th series vol. iii., 1883, p. 429.

in either direction; M M are insulated from K, and from each other by sheets of mica. A plug B closes an aperture in the roof of the furnace, through which material may be introduced from time to time into the crucible. The front and back of the furnace may be closed by sheets of mica held in position by the plates I I, so that the reactions taking place in the crucible may be watched by the experimenter, who must, however, protect himself from the light from the interior by

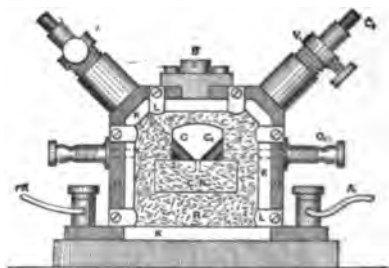


FIG. 73a.

suitable dark glasses. The chamber may be rendered partly vacuous, or may be charged with any particular gas by means of the two tubes O O.

By the aid of such an appliance, and using a current varying from 25 to 450 amperes, with a difference of potentials at the terminals of the furnace of from 45 to 70 volts, Moisson* has succeeded in fusing such refractory substances as lime, and in readily preparing samples of the difficultly reducible metals, such as zirconium, chromium, calcium. He has since† made the furnace reverberatory, by placing the material to be treated in a hollow tube of pure carbon placed at right angles to the electrodes. The heating and electrolytic effects of the arc are thus kept distinct.

* *Comptes Rendus*, vol. cxv. (1892) p. 1031.

† *Ibid.* vol. cxvii (1893) p. 679.

CHAPTER VIII.

MEANS OF SUPPLYING AIR TO FURNACES.

Methods of Producing Draught. — In every furnace it is necessary to conduct away the gaseous products of combustion to enable fresh air to enter and to give up its oxygen to the fuel. This passage of the fire gases from the furnace and of the air to the furnace may be effected in two ways:—First, by exhausting the products of combustion; and, second, by forcing in air for combustion. In the former method, a space containing rarefied air is formed in the furnace, and atmospheric air flows in from outside so as to preserve the equilibrium, whilst in the latter method the pressure in the furnace is greater than that of the air outside, and consequently the air and the fire gases are forced out. Although the current is usually the same in both cases, the influence on the combustion may be different when the movement is effected by the compression or rarefaction of the air.

The exhaustion of the air is usually effected by means of chimneys. The chimney or stack may be regarded as a vertical pipe containing heated and expanded gaseous products of combustion. The column of gas within the chimney is, in consequence of the expansion due to heat, considerably lighter than a column of air of the same height at the ordinary temperature. The consequence is, that owing to the difference of weight, there is an excess of pressure of air under the grate, and movement ensues. This difference in the weight of the hot and cold columns is equal to the weight of the increase in volume that would be produced by heating the cold column of air to the temperature of the chimney. If the elongation thus produced be represented by h , the velocity of the movement $v = \sqrt{2gh}$; but h is dependent both on the height of the cold column of air and on the difference of temperature within and outside the chimney, whence it follows that theoretically the velocity of a current of gas within a chimney increases proportionately with the square root of the height and the square root of the difference of the external and internal temperatures, and that consequently the action of equal increments of height

and temperature becomes continually smaller. But the action of a chimney does not depend so much on the velocity produced as on the weight of air supplied in a given period of time. The higher the products of combustion are heated, when they pass into the chimney, the greater is their volume, and with equal velocity the less weight of gas would actually pass through the same chimney. The velocities, it has been shown, increase with the difference of the external and internal temperatures, but only in proportion to the square roots, whilst the relative weight of the gases decrease in direct proportion to the temperature by $\frac{1}{273}$ of the original volume for every degree Centigrade. There must therefore be a limit where the action of the chimney reaches its maximum, and it has been calculated that this maximum is attained when the difference of temperature amounts to 273° , or, in other words, when the external air is at the mean temperature, and the chimney gases have a temperature of 300° . Similarly it has been calculated that the quantities of air supplied to the chimney between 200° and 400° differ but slightly, so that for the chimney-draught these temperatures appear to be the most suitable, whilst for the utilisation of heat in the furnace the lower chimney temperature is obviously to be preferred, and even when the temperature of the chimney gases is only 100° , the quantity of air drawn in is to that drawn in by a chimney having a temperature of 300° as 7 : 8.

The amount of gas passing out of the chimney could be determined from the height and temperature of the shaft and the specific gravity of the gases, if only the resistance given by friction to the gases in motion and the so-called "free section" were known. The term "free section" is applied to the sum of the areas of the interstices between the lumps of fuel on the grate. The smaller this free section is, the quicker is the motion of the air in it, and the more perfect the combustion, provided that the reduction in section is due to a diminution of the area of the grate and not to undue clogging of the layers of fuel which, by increasing the friction, at once diminishes the action of the shaft as the volume of air supplied is necessarily lessened. For this reason small grates give rapid combustion and large grates slow combustion, with the same chimney. It has, however, previously been shown that a rapid motion of the air, in this case equivalent to rapid combustion, facilitates the production of carbonic anhydride, whilst a slow motion facilitates the production of carbonic oxide. As a rule, therefore, for the production of heat and for high temperature, rapid combustion on a small grate is to be preferred to slow combustion on a large grate.

The height of the stack must increase with (1) the rapidity of the combustion; (2) the height of the layer of fuel on the grate; and (3) the resistance to which the current is exposed in passing from the grate to the foot of the stack. On the other hand, the height of the stack must increase in inverse ratio to the temperature of the evolved gas.

For furnaces in which the combustion is not rapid, and in which there is but slight frictional resistance, as in furnaces from which the gases pass directly to the shaft, the height of the stack need not exceed 33 feet. Welding, puddling and other furnaces, in which the combustion is rapid, require a shaft at least 50 feet in height, if the gases pass into it at a high temperature; but if they are cooled on their way, and have great frictional resistance to overcome by being utilised, before they reach the shaft, for other purposes, as for heating steam-boilers, it is advisable to make the shaft 65 to 80 feet, or even 100 feet if the length of the flues is considerable, and if they are narrow and crooked.

A chimney is frequently arranged so as to be common to several furnaces, and in this the gases from all the furnaces unite. Its section is calculated on the assumption that the minimum velocity of the gases in the chimney ($6\frac{1}{2}$ feet per second) is not exceeded, even if only one of the furnaces be working and the others are cold. At the same time, in order to prevent an unduly decreased velocity when all the furnaces are at work, the common shaft must be made of considerable height, usually 130 to 165 feet. To ensure the successful working of chimneys of this kind, it is important that the up-currents should pass into the shaft in parallel directions, so as to prevent suction being arrested by the impact on each other by converging streams of gases. In order that cold air shall not be drawn into the shaft from a furnace that is not being worked, every flue passing from the furnaces to the shaft must be furnished with a damper.

The vertical projection of the interior of the shaft may be either of the same width above or below, or there may be a slight narrowing at the top. The tapering shape increases the stability of the shafts, especially when they are exposed to the action of storms. It has been proved theoretically that a slight divergence towards the top gives a better draught. The angle at which the sides are inclined to the perpendicular should be 0.5 to 1.5 degree.

Any cooling of the gases interferes with the draught. For this reason brick shafts are preferable to iron ones, and the interior should be made as smooth as may be, so as to lessen friction.

The first researches on chimney gases are due to Péclet, who published some analyses in 1828; but his results and those of different experimenters who followed him, were open to the objection that the samples taken for analysis were only small fractions of the total gases in the flues, and, as they were not taken with sufficient frequency, they could not represent the mean composition. This grave defect was, however, remedied by Scheurer-Kestner in an elaborate research on the composition of the flue gases of boiler furnaces, which will always form the basis of future experiments in this direction.

A series of experiments conducted by this distinguished chemist and Meunier, in 1868, on the combustion of fuel in boiler furnaces, showed the difficulty of burning fuel completely on the grate of a furnace; and the analyses of the gases made by them led to the conclusion that the products of combustion always contain unburned constituents, even in the case of a thin layer of fuel and an excess of air of more than 50 per cent.; that is to say, with volumes of 240 cubic feet of air for every lb. of coal burnt, instead of 128 to 160 cubic feet. They also showed that the mean proportion of unburned hydrogen reached 20 per cent. of the total amount present. This points to the fact that hydrogen is more difficult to burn, even under favourable conditions, than carbonic oxide, and that with a thin layer of incandescent fuel, the unburned carbon in the gas exists more often in the form of a hydrocarbon than in that of carbonic oxide.

In securing a representative sample of gas, the position of the flue from which the gases are withdrawn, is by no means a matter of indifference. With a view to collect soot, it should, of course, be as near to the incandescent fuel as possible; but Cailletet has shown that the gaseous products from furnaces must not be collected immediately after being liberated from the fuel, for a current of gases from a mass of incandescent fuel may contain notably more carbonic oxide than the same gases do when cold—that is, during the cooling, combination of carbonic oxide and oxygen takes place.

In a series of tests made by the author* in connection with an exhibition opened with a view to abate the nuisance arising from smoke, 85 cases showed that the relation by weight between the carbon completely burnt to carbonic anhydride, and that present in the form of hydrocarbons or carbonic oxide, varies between the limits of 1000 : 4 and 1000 : 375. There were, how-

* *Report of Smoke Abatement Committee*, London, 1882, in which volume there are references to the literature of the subject.

ever, only 9 cases in which a ratio of 1000 : 200 was exceeded, and but 3 in which the ratio was less than 1000 : 10.

In 17 cases given by Scheurer-Kestner, this relation varied from 1000 : 10 to 1000 : 211, the result being mainly dependent on the amount of air introduced to effect the combustion. With reference to the hydrogen, it is to be observed that in these experiments, the proportion of carbon completely burnt to carbonic anhydride to the hydrogen present either in the free state or as hydrocarbons, varies from 1000 : 3 to 1000 : 16. The loss of carbon in the form of soot never exceeds 1 per cent. of the fuel burnt, while the mean loss is probably between 0.5 and 0.75 per cent.*

Blowing Engines.—The mechanical appliances employed for the production of a stream of compressed air are so varied in their details that it is impossible to do more than allude to them, the construction and the principles involved falling more in the province of the mechanical engineer than in that of the metallurgist.

In early times the blast was obtained solely from leathern bellows, which were at first single-acting and subsequently double-acting, but as leather soon becomes inflexible and brittle, it was found advisable to employ wooden bellows. In this way was evolved the box-blower, with single-acting movement of a piston. In the course of time cast-iron was substituted for wood, and the iron blast-cylinder, one of the forms of blowing engines still in general use, was obtained. In addition to this, for low pressures and large volumes of blast, fans and blowers are largely used.

A blowing cylinder consists of a cast-iron cylinder fitted with a piston receiving a reciprocating motion from the crank-shaft of the engine. At every stroke air is drawn into the cylinder on one side, and on the other compressed air is forced into a reservoir or into the blast-main. The interior of the cylinder is connected with the atmosphere on the one hand, and with the blast-main or reservoir on the other, by means of flap- or disc-valves fitted in the cylinder-covers. The piston is actuated by engines of the vertical direct-acting, or of the beam-engine type, the former being now generally preferred. On the Continent the blowing engines are frequently of the horizontal, direct-acting, condensing or compound class. The amount of blast required to be delivered is often very considerable, as is shown by the following examples :—

* For fuller information on this subject the student is referred to Gruner's *Traité de Métallurgie*, and Ledebur, *Die Oefen*.

The celebrated blowing engine at Dowlais, in South Wales, has a blowing cylinder 144 inches in diameter, and a stroke of 144 inches. The areas of the admission and discharge valves are 56 square feet and 16 square feet respectively, the former being equal to half the area of the piston. The steam-cylinder is of 55 inches diameter, and its piston has a stroke of 13 feet. The volume of blast delivered is 51,000 cubic feet per minute, at a pressure of $3\frac{1}{2}$ lbs.

At Newport, near Middlesborough,* there are four direct-acting blowing engines, with steam cylinders of 32 inches, and blowing cylinders of 66 inches, and 4 feet stroke. These are supplied with steam at a pressure of 55 lbs. per square inch by eight Cornish boilers, fired by waste gas, 35 feet long and $5\frac{1}{2}$ feet in diameter, with an internal flue of $2\frac{3}{4}$ feet in diameter. The engines make twenty-four revolutions per minute, and deliver 8000 cubic feet of blast per minute to each furnace, at a pressure of $4\frac{1}{2}$ lbs.

At the Lucy furnace in Pittsburgh, where the greatest out-turn of iron for one day was 340 tons, for one week 1946 tons, and for one month 7919 tons, the diameter of the blowing cylinder is 84 inches, that of the steam cylinder 42 inches, the length of stroke 60 inches, and diameter of fly-wheel 24 feet.†

For foundry purposes the blast is usually supplied by centrifugal fans or by blowers. The fan, although possessing the advantage of great simplicity, has but limited application, since it is useless when pressures exceeding about 6 inches of water-column are required to be produced. In such cases, the Root's blower, or a machine of similar type, may be advantageously employed. It consists of an iron casing, in which are placed a pair of revolving cast-iron wafers driven by belts off pulleys, and making about 400 revolutions per minute, the smallest possible clearance being left between the two curved surfaces as they revolve.

The blast is conveyed in air-tight rivetted sheet-iron or steel pipes or *mains* of ample cross-section, to the hot-blast stoves.

Hot-blast Stoves.—The temperature of combustion increases with the temperature of the air consumed up to the limits which are fixed by dissociation. Hot air economises, in the blast-furnace, a sum of *calories* equal to that which it brings, but if this heat has to be initially imparted to the air by the combustion of a fuel of equal value to that consumed in the furnace, it is

* *Journ. Iron and Steel Inst.*, vol. i., 1887, p. 92.

† *Ibid.*, 1888, No. i. p. 311.

evident that the economy will be at best but doubtful. In all cases the advantage of hot blast will be in direct proportion to the cheapness of the fuel that is burnt in heating the blast. There is a great advantage when the waste heat of the furnace can be utilised in this way. By employing a fuel identical with that burnt in the blast-furnace, it would appear, however, that there is still a distinct advantage due to the more perfect combustion of the carbon that is attained in the furnace, there being produced a greater proportion of carbonic anhydride as compared with that of carbonic oxide.

The apparatus in which the blast is heated before passing to the furnace is heated by solid fuel or by the waste gases from the furnace.

Two substances are employed to transfer the heat. These are iron and fire-brick. The first appliances for heating the blast date from 1828, when they were introduced by Neilson at Glasgow. This discovery, that 100 lbs. of coal burnt in heating the blast was able to save 300 or 400 lbs. of fuel burnt in the furnace, was received with disbelief, and ironmasters were very slow in availing themselves of one of the most important inventions which had been made in connection with the metallurgy of iron.

The cast-iron hot-blast stoves now used in metallurgical works may be referred to two types, both introduced at the same date. In 1833 Faber du Faur invented a hot-blast stove, consisting of sixteen cast-iron pipes united by semi-

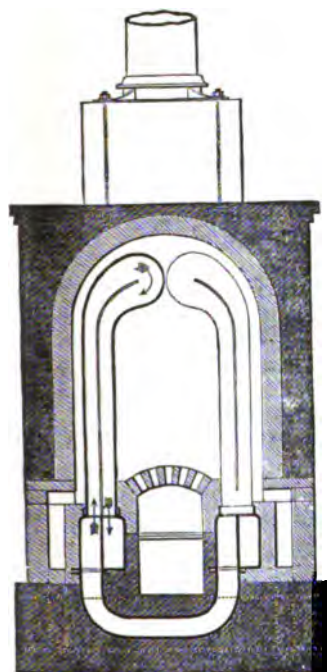


FIG. 74.

circular bends, forming one long serpentine pipe enclosed in a chamber heated by the waste gases from the blast-furnace. It was placed directly above the throat of the furnace. The second type of iron hot-blast stove differs from the former in that the blast-current is split in its passage through the stove. It consists of an oblong fire-brick chamber, containing a series of

A-shaped cast-iron pipes, that connect two parallel horizontal main pipes, embedded in the masonry on either side of the rectangular fire-place that extends throughout the stove.

A modification of this second type is the so-called pistol-pipe stove (Fig. 74). In this case the arch is replaced by a single pipe divided longitudinally, the division reaching nearly to the top, which is enlarged in the form of the stock of a pistol.

Two types of regenerative hot-blast stoves are employed. These are based on the principle of the intermittent absorption of heat by masses of fire-brick and the transference of the heat to the blast. The first stove of this type was constructed by Cowper in 1860; it is similar in arrangement to a Siemens regenerator. It is enclosed, however, in an iron case so as to withstand the pressure of the blast. The first stove of the second type was constructed by Whitwell in 1865 for the Thornaby works at Stockton. It is essentially a serpentine pipe-stove constructed of fire-brick.

The Cowper stove, which is represented in sectional elevation and plan in Figs. 75 and 76, consists of a sheet-iron tower I, of circular horizontal section, closed with a dome-shaped roof B, and lined internally with fire-brick. A circular flame-flue F, extends from the base to the dome, whilst the remainder of the stove is filled with fire-brick chequer-work, and forms the regenerator R. The waste gases from the blast-furnace pass in by the valve G, and are burnt at N, the necessary air for combustion entering by the valve A. The flame descends through the chequer-work and passes out by the chimney-valve V. In this way the brickwork becomes heated. The valves G, A, and V are closed, and cold blast, admitted through the valve C, is passed through in the reverse direction. It absorbs heat from the chequer-work and is delivered as hot-blast by the valve H. The chequer-work is constructed of Cowper's honeycomb bricks. Two stoves are worked in conjunction, one being heated while the blast passes through the other. It is advisable to have a third in reserve. These stoves are 40 to 65 feet high and 26 to 28 feet in diameter. Compared with pipe-stoves the saving of fuel is about 20 per cent. and the increased make is also 20 per cent. An exact average of over 100 stoves shows the saving in fuel to amount to a little over 5 cwt. of coke per ton of iron.* In 1883 there were 360 of these stoves at work in Europe and America.

The Whitwell stove is shown in Fig. 77. It is merely a brickwork serpentine pipe formed by vertical walls, and enclosed in a cylindrical case. The waste gases from the furnace enter

* E. A. Cowper, *Journ Iron and Steel Inst.*, 1883, p. 576.

at A and are burnt, air being admitted through the passages *a, a*. The flame passes up and down the passages formed by the dividing

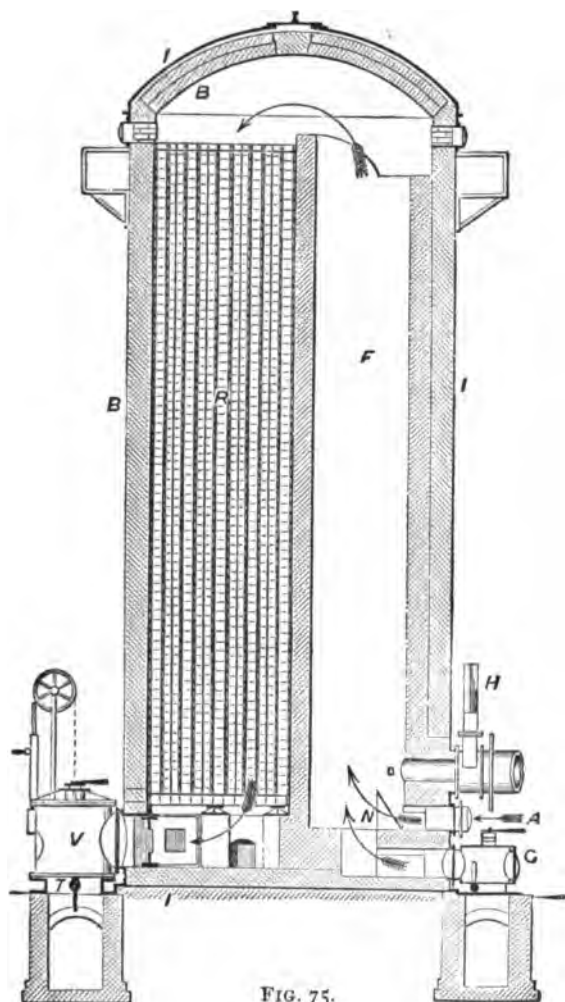


FIG. 75.

walls, and escapes to the chimney by the passage C. When the stove is heated, the gas and chimney valves are closed, and

cold blast is admitted at D, and passes out heated at B. The walls forming the regenerator consist of 5-inch brickwork. The

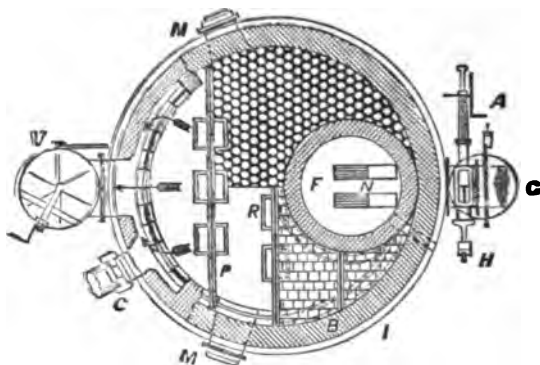


FIG. 76.

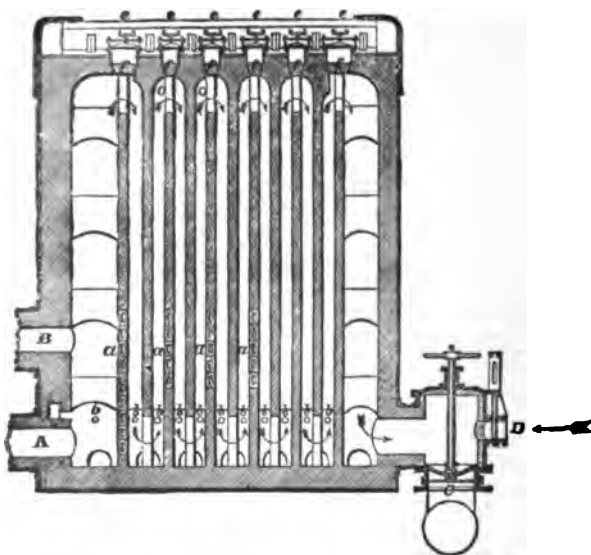


FIG. 77.

older forms of Whitwell stove were 25 feet in height. Recently the height has been greatly increased, the largest size adopted

being about 70 feet high and 25 feet in diameter. A domed top is now used.

The relative merits of fire-brick and iron hot-blast stoves may be seen from the following comparison drawn by Lürmann :*—

Fire-brick stoves may be heated to very high temperatures without interfering with their working, if the dust contained in the blast-furnace gases contains no basic constituent which has a detrimental action on the fire-brick.

The heating surface of fire-brick stoves must be considerable if the temperature of the blast is not to be altered too rapidly, and if the working is not to be interrupted too often. The cost of erection of these stoves is consequently high. The cost of maintenance, on the other hand, is very low.

The older forms of fire-brick stoves are not easily cleaned. By rendering cleaning possible, the construction becomes more complicated, and the cost is consequently increased.

Fire-brick stoves require a skilled attendant, as the working is intermittent.

Iron stoves can only be heated to the temperature at which the cast-iron, of which they are made, softens.

Iron stoves, with sufficient heating surface for the amount of blast to be heated, necessitate a smaller expenditure of capital than the older forms of fire-brick stoves, and give uniform temperatures. They, however, present the danger of the working being interfered with on account of pipes having to be replaced, and consequently the cost of maintenance is high. On the other hand, the value of the worn-out material of the iron stoves is higher than that of the fire-brick ones.

Iron stoves are easily cleaned.

Iron stoves may be entrusted to the ordinary workmen, and demand no special skill.

Fire-brick stoves, as compared with those of iron, possess the advantage of effecting a saving in heat by lowering the temperature at which the products of combustion enter the chimney. The quantity of coke consumed when fire-brick stoves are employed being less than when iron stoves are used, the weight of furnace gases is correspondingly affected. Sir Lowthian Bell † assumes that for 20 units of iron made there are 122 units of gas in the former against 129 units in the latter. Allowing 10 per cent. of free atmospheric air in the burnt gases as they leave the stoves, their weight may be taken at 212 and 240 units respectively per 20 units of iron produced. The two accounts may be stated as follows :—

* *Stahl und Eisen*, 1882, p. 361.

† *Journ. Iron and Steel Inst.*, 1883, p. 119.

FIRE-BRICK STOVES.

Heat from combustion of furnace gases	83,700 <i>calories</i>
Less loss of sensible heat in products of combustion—212 wt. \times 189° temp. \times 0.24 sp. ht.	= 9,616
Allow loss of 10 per cent. for radiation =	8,370
	<hr/> 17,986
Leaving available	65,714
Contained in blast	16,018
	<hr/>
Leaving for other purposes	49,696

IRON-PIPE STOVES.

Heat from combustion of furnace gases	88,500 <i>calories</i>
Less loss of sensible heat in products of combustion—240 wt. \times 624° temp. \times 0.24 sp. ht.	= 35,942
Allow loss of 10 per cent. for radiation =	8,850
	<hr/> 44,792
Leaving available	43,708
Contained in blast	11,584
	<hr/>
Leaving for other purposes	32,124

Whether heated in brick or in iron stoves, the blast is conveyed to the furnace in mains lined with fire-brick.

CHAPTER IX.

THERMO CHEMISTRY.

THE great importance of thermo chemistry in relation to metallurgy is becoming so evident, that it is absolutely necessary for the student to have such knowledge as will enable him to consult with advantage the original memoirs of Andrews, Berthelot, Julius Thomsen, Nernst and others. In this country little attention has hitherto been devoted to thermo chemistry in relation to metallurgical teaching, but in France admirable work has been done, notably by Ditte,* in bringing within the reach of students the results of the labours of Berthelot and of St. Claire Deville.

Ostwald reminds us that chemical energy is the least known of all the various forms of energy, as we can measure neither it nor any of its factors directly, the only way of obtaining information regarding it is to transform it into another species of energy. It passes most easily and completely into heat, and the branch of science which treats of the measurement of chemical energy in *thermal units*, is called thermo chemistry. The quantities of heat evolved or absorbed measure the decrease or increase of chemical energy in so far as other energy is not involved in the process. The ordinary equation of the chemist $C + O = CO$ is far from representing the whole truth, for in fact, C unites with O, to form an entirely new body (CO) which may be liquid, solid or gaseous, but it never has the same potential energy as was possessed by the bodies from which it was formed. The equation should therefore be $C + O = CO + q$ *heat units*.

It must be remembered that only the final result of a chemical process can be measured. The calorimeter is the instrument used in thermo-chemical measurement. First as regards the "calorie" employed. The student will remember that the calorific power of carbon in the form of charcoal as determined by the aid of the calorimeter is given on p. 122 as being 8080, that is 8080 units (grammes) of water will be heated from 0° to 1° by the complete

* *Leçons sur les Métaux.* Paris. 1891.

combustion of 1 unit (1 gramme) of carbon. The calorie hitherto employed in this book is, however, too small for use in thermochemical measurement. The heat required to raise 1 kilogramme of water is the unit employed in this chapter. It must be borne in mind that *the quantities of energy and heat given in thermal equations refer to such quantities of the substances as amount to their formula weight in grammes.*

Hence the thermal equivalent of carbon burnt to carbonic anhydride is 97. The calorific power of charcoal being 8080 it may be well to show how the number 97 is deduced. In the equation $C + 2O = CO_2$, 12 grammes of carbon (its equivalent weight) are used. 8080 represents the unit of carbon, hence $8080 \times 12 = 96,960$, but the thermo-chemist, as above stated, employs 1000 grammes as the unit of water instead of 1 gramme, and the sum becomes $\frac{96,960}{1000} = 96.960$ or in round numbers 97.

The various forms of calorimeter are fully described in the works to which reference is given at the end of this chapter. The form of the calorimeter is modified to suit the particular conditions of the experiment, but the limits of this book will only permit a brief reference to the methods by which the calorimetric determinations, given in the accompanying table, were made. (See Folding Plate placed at the end of this chapter).

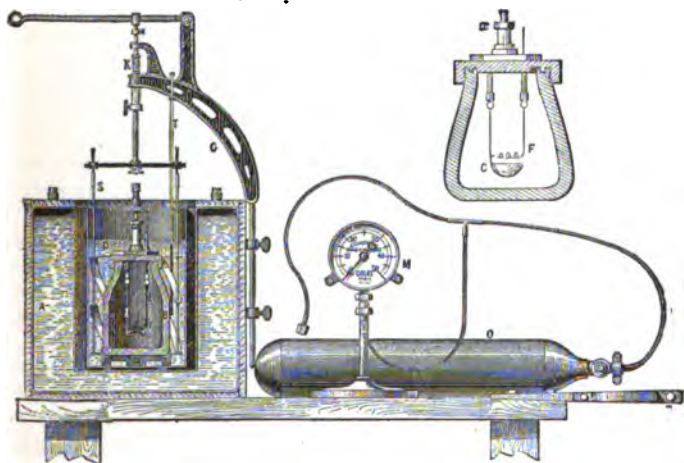
The calorimeter employed by Berthelot is a thin cylindrical vessel of platinum, of about 600cc. capacity. If, for instance, the problem is to determine the heat evolved by the reaction between two liquids these would be placed in flasks of very thin glass of about 300cc. capacity provided with short necks marked with the calibration line at the base of the neck. These receptacles are allowed to stand near the calorimeter until they acquire a constant temperature which is carefully measured. The difference in temperature between their contents should not exceed $\frac{1}{10}$ th of a degree. The contents of one flask would then be poured into the inner chamber of the calorimeter, and rapidly stirred with the thermometer, the temperature is then noted, and the contents of the second flask are added to the liquid already in the calorimeter, and careful thermometric observation is made to ascertain whether the admixture has been attended with a lowering or an elevation of temperature. The above description has merely been given to indicate the general nature of the method, but treatises on calorimetry must be consulted with reference to the precautions to be observed when solids and liquids react, or when the reaction between gases and liquids has to be studied.

Bomb Calorimeter.—The instrument, of which a description

will now be given, is the one in use in the author's laboratory. It often happens that the metallurgist has to deal with reactions which are attended with vivid combustion—the reaction, for instance, between solids and gases—the product of which is gaseous, and in such cases closed combustion chambers are employed, and the heat is not measured directly by a thermometer, but is transferred, through the walls of the combustion chamber, to water contained in a receptacle in which the combustion chamber is placed. There are various forms of such combustion chambers, but the one most serviceable to the metallurgist is the modification of Berthelot's bomb calorimeter devised by M. Mahler, and the following description shows the nature of

FIG. 77a.

FIG. 77b.



the appliance and the method of using it. The apparatus consists essentially of a shell or bomb, B (Figs. 77a and 77b), forged out of high-class mild steel, having a capacity of 654 c.c. (say 40 cub. in.), and weighing about 4 kilogrammes (or $8\frac{1}{2}$ lbs.) with its accessories. The shell, B, which is 8 millimetres ($\frac{5}{16}$ inch) thick, is nickelised on the outside, and enamelled inside, so as to withstand the corrosive and oxidising action of combustion; but the coating of enamel does not sensibly interfere with the transmission of heat. The shell is closed by a screw cap, tightened on to a lead ring; and the cap is provided with a conical screw cock (x, Fig 77b), for the introduction of oxygen. A platinum rod, attached to the cap, holds the capsule, C, on which is placed the fuel to be tested; and

the latter is ignited by being brought into contact with a spiral of iron wire, F, heated by an electric current. It may be well to assume that the material is either carbon or hydrocarbon, which is to be burnt in oxygen.

The sample to be tested is introduced into the steel bomb, which is then closed, and charged with oxygen under pressure, and the whole apparatus is immersed in the water of the calorimeter. If the fuel be then ignited by the aid of a wire heated to redness by an electric current, it will burn completely and almost instantaneously, the water formed by the combustion of the hydrogen being condensed on the inside surface of the bomb. The heat disengaged by the explosion is transmitted, without any loss whatever, to the water of the calorimeter, and may easily be estimated, while, on account of the rapidity of the operation, most of the usual corrections, such as those relating to the evaporation of the water and variations of the surrounding temperature, may be neglected. The pressure of oxygen is determined by the condition that combustion must always be complete, and that an excess of oxygen is indispensable.

For testing a solid or liquid fuel, a gramme of the substance is placed in the capsule, and the cap is screwed down tightly. Oxygen, under pressure, is allowed to enter by the cock, until the manometer M, shows that a suitable pressure is obtained, generally from 20 to 25 atmospheres. Care must be taken, especially with coal in a finely divided state, to prevent the sample from being displaced, in which case there would be danger of part escaping combustion. The shell thus prepared is placed in the calorimeter, D, which contains a known quantity of water, when the thermometer T, is adjusted, and the helicoidal agitator, S, set to work for a few minutes, to bring the whole apparatus to the same temperature, when all is ready for the observation. In order to prevent irregular loss of heat by the calorimeter, D, it is placed upon three small pieces of cork within a large, metallic, double vessel of water, A, covered externally with a thick layer of felt and provided with a thermometer. This vessel serves also as a support for the bracket G, from which the stirrer S is suspended, and to which the handle and spring K, for working the stirrer, are fixed. O is the vessel containing the supply of oxygen, and E is a clamp in which the bomb may be fixed and prepared for the experiment.

The temperature is noted every minute for four or five minutes, and then the charge is fired by electricity. Although the combustion is almost instantaneous, the transmission of heat to the water requires a few minutes. The temperature is noted, first half a minute, and then one minute after the ignition, and afterwards

every minute, until the thermometer begins to fall, which shows that the maximum temperature has been reached; after which the observations are continued for about five minutes more. The principal elements of the calculation are thus afforded, and especially the one correction necessary, which is due to the loss of heat sustained by the calorimeter before reaching the maximum temperature. The agitator, S, must be worked regularly during the observation, at the conclusion of which the shell is removed from the calorimeter, the cock is opened, and then the shell itself. The inside of the shell is washed with a little distilled water, so as to collect the acid liquid formed during the explosion. The amount of acid is determined by titration.

It is advisable, when experimenting on substances poor in hydrogen, like coke, and consequently incapable of furnishing by combustion sufficient water to form nitric acid, to put a little water at the bottom of the bomb.

For determining the calorific value of a gas of constant volume, a vacuum is made in the bomb, the exact cubic contents of which is known. The bomb is filled with the gas; a fresh vacuum is produced by exhaustion until the pressure is only a few millimetres of mercury, and the bomb is filled with the gas at the atmospheric pressure, and temperature of the laboratory, and the operation is completed in the same manner as with solid and liquid fuels.

The significance of the thermal data, given in the table, which has been obtained by one or other of the calorimetric methods, will now be considered.

It is assumed that the student is familiar with the theory of the granular structure of matter, and with the molecular theory of gases. He must also know that the atoms of every element have valencies of their own, and further that there may be distinct movements and reactions between the atoms arranged in a molecule. The question naturally arises, why do certain reactions take place while others do not? Berthelot held "that every chemical change which can be accomplished without the aid of a preliminary action or the addition of energy from without the system, necessarily occurs if it is accompanied by a disengagement of heat." Viewing a reaction generally, he held that if external energy is not imparted to a system the tendency will be to form that compound, the production of which is accompanied by the evolution of the maximum quantity of heat. It is true that changes resulting in a positive calorific effect occur more often than those accompanied by negative ones, but it is well known that of two or more possible reactions, the one which is accompanied by the evolution of most

heat is not always the one which actually occurs. Decompositions accompanied by negative calorific effects are more frequent at high than at low temperatures. In this connection it must be remembered that heat is not the only form in which energy can be lost by a changing chemical system, as the change may give rise to electrical phenomena. A redistribution of atoms in the molecule may take place, and although the energy is not lost to the system it may not be possible for it to directly appear as heat. In some cases the only outward sign of change is the passage of an element from a normal to an allotropic modification.

Van't Hoff* has pointed out that modern chemical theory had two weak points: it expressed itself neither as to the relative position of the atoms nor as to their movement. It is known that many active organic bodies lose their activity by being heated, and this fact, which is recognised as being of much importance in organic chemistry, can hardly be without significant relations in the inorganic reactions with which the metallurgist has to deal.

The atoms in the molecule have, as has already been stated, movements of their own, and, as Lothar Meyer has urged "if these movements of the atoms are to be considered, then we must investigate what part in the observed calorific effects is to be attributed to them, and how much is due to the potential energy of the hypothetical force of affinity. It is doubtful, however, whether the atoms do possess powers of attraction and consequently potential energy; it is more probable that the whole of the kinetic energy the atoms give out is already their own as such." But suppose atoms do possess "potential energy" of their own to which they owe their "affinities," then when the system undergoes change which satisfies the affinities of the atoms without the addition of energy from an external source, this change must be attended by a "locking up" of energy which must have been kinetic, and consequently there is less kinetic energy available in the system to appear as heat, so that although in a particular reaction but little heat may be evolved, there may nevertheless be a considerable degradation of chemical energy.

In chemical operations generally, and especially in metallurgical ones, there is another consideration of much importance. If two compound bodies react one upon the other, the presence of the products of the reaction will bring it to an end, and a state of equilibrium will be established, so that both the original and the newly formed substances are present in definite quantities that

* *La Chimie dans l'espace* (original edition).

the 1990s, the number of people in the world who are under 15 years of age is expected to increase from 1.1 billion to 1.5 billion. The number of people aged 65 and over is expected to increase from 200 million to 400 million. The number of people aged 15 and over is expected to increase from 3.5 billion to 4.5 billion. The number of people aged 15 and over is expected to increase from 3.5 billion to 4.5 billion. The number of people aged 15 and over is expected to increase from 3.5 billion to 4.5 billion.

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lead, by the aid of zinc. H. Roessler and Endelmann have recently shown that aluminium has a remarkable effect in protecting the zinc from loss by oxidation, and, further, the presence of one-thousandth part of aluminium in the zinc is sufficient to exert this protecting action on that metal.

An examination of the following thermal equations and the remarks which precede them, will show how frequently, in conducting metallurgical operations, demands are made upon energy, in the form of heat, from a source external to the particular "chemical system" which is undergoing change. It has been urged that if it is the energy of the external heat which dissociates a compound and enables a reaction to take place, then chemical equilibrium such as is revealed by experiments on dissociation, is really equilibrium between the energies of affinity and of heat. It follows, as M. Duhem* has pointed out, that the third law of thermo-chemistry is greatly weakened, if not rendered absurd, by the necessity for bringing external heat to a chemical system. This law states that, "Every chemical change which is accomplished without the intervention of external energy, tends towards the production of a body which evolves the most heat." If it be necessary to import external heat, the law admits of being reduced to the useless expression, "Every reaction which does not absorb heat evolves it."

But the more ardent members of the school of Deville, which has rendered such splendid services to metallurgy and to physics, do not advocate the employment of the mechanism of atoms and molecules in dealing with chemical problems, but would simply accumulate evidence as to the physical circumstances under which chemical combination and dissociation take place. They do not even insist upon the view that matter is minutely granular, but, in all cases of change of state, make calculations on the basis of work done, viewing "internal energy" as a quantity which should reappear when the system returns to the initial state; and they view chemical combination and dissociation as belonging to the same class of phenomena as solidification, fusion, condensation, and evaporation. As yet the study of chemical equilibrium is not sufficiently advanced to afford a basis for building a theory of metallurgy, and, moreover, enough has been adduced in this book to show the author's belief in the existence of molecular movement and atomic grouping, and if there is evidence of the existence of atoms and molecules it is not advisable to ignore their existence when dealing with metallurgical problems.

* Duhem, *Introduction a la Mécanique Chimique*, Paris, 1893, p. 79.

There is one important theorem developed by M. Moutier which must not be overlooked. He has shown that under a given pressure there is only one temperature at which transformations are reversible. If the conditions of equilibrium are such that the transformation occurs below the critical temperature, it is attended with evolution of heat, while, on the other hand, if the transformation occurs above this temperature, it is attended with absorption of heat. Take the case of a mixture of carbonic anhydride, lime and calcium carbonate, exposed to such a pressure and temperature that the system is in equilibrium. It is stable, more carbonic anhydride cannot combine with the lime, nor can fresh calcium carbonate be decomposed. But destroy the equilibrium by an elevation of temperature, carbonic anhydride and lime will be the result, but the reaction is attended with absorption of heat. On the other hand, destroy the equilibrium by lowering the temperature, lime and carbonic anhydride will combine, and the reaction will be attended with an evolution of heat. According to this law, the occurrence of a definite chemical change will not be determined by the fact that much or little work would be done (law of maximum work), but by the relation between the temperature and pressure to which the substances are subjected. This, and other theorems of Moutier, apply, however, only to reversible reactions, and the student should be warned that the theorems as to the conditions of chemical equilibrium lead in many cases to the expectation of reactions or transformations which are not found to occur exactly as anticipated. Thus reactions occur suddenly at an abnormally high temperature, and with explosive violence, whilst the theory of chemical equilibrium indicates that reactions should tend to check themselves, and that therefore there should be no tendency to explosion. Other cases are presented by the phenomena of surfusion, supersaturation, and delayed ebullition. It would thus appear that a position of *unstable* or *false* equilibrium may be established, but if the equilibrium be destroyed, it may be by a further rise in temperature, by the presence of a minute trace of impurity or even by a mechanical shock, the change is propagated rapidly through the mass.

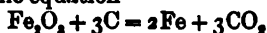
Thermo-chemists are reproached for having neglected the study of reactions at high temperatures, for the measurement of which, until recently, no simple methods were available, but now, as has been shown in these pages, that high temperatures can be measured with facility, it is to be hoped this reproach may be removed. When this is done, it will be interesting to compare the new thermal equations representing reactions at high temperatures with those now in use. Such an investigation will be very tedious,

but there are many reactions at high temperatures the study of which can be undertaken, though they present great difficulty.

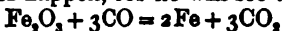
The student may fairly ask why a series of equations are presented which are confessedly based on numbers that were obtained from experiments conducted at temperatures differing from those employed in practice. The answer is that these equations do enable him to know the quantity of heat that will be required to obtain a certain result, and also indicate the probable temperature at which an operation can be effected. - A reaction, the final result of which is represented by a minus number which is large when considered in relation to the quantity of material involved, generally means that a high temperature is necessary to effect it, but much will depend upon the melting points of the members of the particular chemical system.

A reaction between sulphide of lead and sulphate of lead is attended with a large absorption of heat (-180 large units), the mass involved being considerable. The reduction of ferric oxide by carbon is attended with an absorption of heat (-112 large units). Both these reactions require very high temperatures, the mass in the latter case is relatively small, but the melting point of the reduced iron is high.

The ordinary atomic equation



shows that the reduction of one ton of ferric oxide should be effected by four and a half hundredweights of carbon, leaving the CO produced to reduce still more ferric oxide. The thermal equation, with its very large minus number (-112), prepares the student for the fact, well known to the blast furnace manager, that the reduction of one ton of ferric oxide in accordance with the above equation is a very difficult operation, which would require a large amount of fuel, and, moreover, the student is led to expect that the reaction represented by the above equation is evidently not the one that does happen, for he will see that the reaction



which is accompanied by a disengagement of heat ($+4.6$) is probably the main reaction that takes place in the blast furnace.

Whenever an equation shows that a reaction is accompanied by the evolution of much heat, it is safe to conclude that it will take place either at a low temperature, or will be effected with ease.

Thermal Equations.—In using these, the student must bear in mind that all compounds that have to be decomposed will absorb as much heat during decomposition as they evolved while they were being formed, so that it is necessary to take the algebraic sum of each side of the equation, and to algebraically

subtract the total heat required to effect all the decompositions, from the total heat evolved from all the combinations. The difference will be the total quantity of heat evolved or absorbed, according to its particular sign. If the answer has a plus sign then there is an evolution of heat, if a minus one, then there has been absorption of heat. For example take the following equation :



Here two molecules of plumbic sulphate and two molecules of plumbic sulphide have to be decomposed, whilst two molecules of plumbic oxide, three molecules of sulphurous anhydride, and one molecule of plumbic sulphide are formed. Then

Total heat required for decomposition.		Total heat evolved by combination.	
PbSO ₄	2 × 216.2 = + 432.4	PbO	2 × 51.0 = 102.
PbS	2 × 17.8 = + 35.6	PbS	1 × 17.8 = 17.8
		SO ₂	3 × 71. = 213.
	<hr/>		<hr/>
	+ 468.0		+ 332.8
	<hr/>		<hr/>
Total heat evolved by the members of the system		= + 332.8	
Total heat originally absorbed when the members		} = + 468.0	
of the old system were formed			
		<hr/>	
Difference, or the quantity of heat as would be		} = - 135.2	
measured by the calorimeter			
		<hr/>	

It will be seen that this reaction is accompanied by an absorption of heat, and is thus endothermic.

But it must be remembered that this calculation, to be rigorously accurate, ought to be corrected to the exact temperature at which the reaction occurs. The folding plate gives the numbers obtained by heating up the chemical system to the temperature at which reaction occurs, then allowing the reaction to take place, and subsequently cooling the system to the initial temperature. Unfortunately, sufficient data as to the specific heats of various bodies at high temperatures have not as yet been accumulated to enable this to be done, but the correction to be made is as follows :

Let M_1 , M_2 , &c., be the respective masses of the reacting bodies :—

$M_a, M_b, \&c.$, be the respective masses of the products of the reaction,

$S_1, S_2, \&c., S_a, S_b, \&c.$, be the mean specific heats of the different masses, over a range of the temperature, t , of the water in the calorimeter to the temperature, T , of reaction,

T = the "temperature of reaction," or that temperature at which the reaction can proceed,

N = number of heat units as measured under the standard conditions in the calorimeter,

and let C be the true value required,

then $C = N + (T - t) [(M_1 S_1 + M_2 S_2 + \&c.) - (M_a S_a + M_b S_b + \&c.)]$

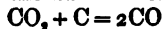
In turning to the modern aspects of metallurgical practice, we shall see that the whole range of the metallurgist's field of study is changing. It is no longer possible for him to devise a series of operations on the evidence afforded by a set of equations which indicate the completion of an operation; he has, as has already been suggested, to consider the complicated problems which have been introduced into chemistry from the sciences of physics and mechanics. He has, in fact, no longer to deal merely with atoms and molecules, but with the influence of mass. If metallurgists are to advance their industrial practice, they must think in calories, and not merely employ the ordinary atomic "tools of thought." They will then be able to suggest what reactions can, under given conditions, take place; to indicate those which will be completed; and to avoid those that are impracticable.

In order that the application of the preceding observations may be evident, it will be well to consider briefly the two main operations upon which metallurgical practice is based.

These are (1) the reduction of oxides by carbon and by hydrogen (see *ante*, p. 223), and (2) the oxidation of metals by an oxidising agent, usually air (*ante*, p. 224).

First, as regards the reducing action of carbon, reference to the table (p. 304) shows that the heat of combination of carbon and oxygen into carbonic anhydride, CO_2 , is 97 large calories, but in the blast furnace in the presence of excess of carbon, carbonic anhydride is converted into the main reducing agent, carbonic oxide, by the very well-known reaction, $CO_2 + C = 2CO$.

The carbonic anhydride, in combining with carbon to form carbonic oxide, becomes doubled in volume. If, however, the equation be completed by the addition of the thermal equivalents:

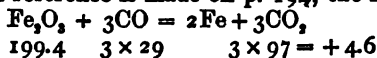


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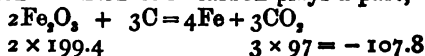
$29 \times 2 = -39,$

it will be seen that this reaction, one of the fundamental ones in the whole range of metallurgy, is really accompanied by an absorp-

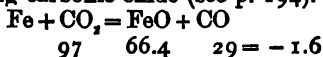
tion of heat—that is, it is endothermic, and would, by Bertholet's law, be impossible, if heat external to the chemical system were not available. In the blast furnace there is such external heat, which acts in two ways: (1) by "depolymerising"—that is, simplifying the atomic constitution of the carbon, which can then combine with the oxygen of the CO, with evolution of more heat than from carbon in its normal condition; or (2) by dissociating the carbonic anhydride, thus setting oxygen free which is in a specially favourable condition to combine with the carbon and so form the main reducing agent, carbonic oxide. In the case of the reduction of iron, to which reference is made on p. 194, the reaction,



is exothermic, that is, attended by evolution of heat, but there is another reaction in which solid carbon plays a part,

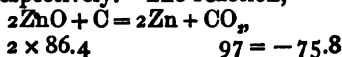


This is strongly endothermic; how then can the reduction of oxide of iron by the occurrence of this reaction be explained? The calorific power of carbon varies with its mode of aggregation; in the diamond form it evolves 94 calories in burning to CO₂, while the amorphous variety yields 97 calories. It may be that the heat of the furnace depolymerises the carbon, and if it is brought to such a molecular condition that the heat of formation of carbonic anhydride from it is 117 instead of 97, then the endothermic equation would become an exothermic one. This is not at all an extravagant supposition, for it has been estimated that if carbon could be burnt as gaseous carbon, the heat of formation of carbonic anhydride would be no less than 136.0. We have, moreover, no knowledge, as yet, of the molecular form of the liberated iron. There is, however, another point to be considered: metallic iron will, as is well known, decompose carbonic anhydride, becoming oxidised itself and forming carbonic oxide (see p. 194). The equation is,



It will be seen, on comparing this with the last equation but one, that the amounts of heat are very nearly balanced, +4.6 in the one case and -1.6 in the other, and when this is the case the inverse reaction may very readily be brought about by comparatively slight variations in the external conditions.

Two interesting cases may be borrowed from the metallurgy of zinc and of lead respectively. The reaction,



occurs in the presence of excess of carbon which splits up the carbonic anhydride formed; but it is strongly endothermic as is also the reaction, $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2 = -18.4$; the latter is, however, less endothermic than the former. It is nevertheless the fact that when zinc oxide and carbon are introduced into a retort which is strongly heated, zinc is reduced in abundance (this is the main method adopted in the metallurgy of zinc), carbonic anhydride together with some carbonic oxide being the result. How is this reduction to be explained? Possibly the carbon under the influence of external heat loses its condensed form and assumes one analogous to that in which carbon exists in carbonic oxide, so that during the passage from the system, $\text{ZnO} + \text{C}$ to $\text{CO} + \text{Zn}$, all the heat is absorbed. The part played by the external heat is twofold: it furnishes the energy necessary to depolymerise the carbon, it may also modify the specific heats and heats of formation of the bodies in presence of each other. Dissociation also plays an important part (*see ante*, p. 301).

It will be evident that of the two reactions given above, the one in which carbonic oxide and oxide of zinc react is endothermic (-18.4), but less so than that in virtue of which carbon acts on the zinc oxide (-75.8). The passage from one set of reactions to the other may be effected by the presence of even a minute quantity of air entangled in the mixture of ore and carbon introduced into the retort. First, the oxygen in the air may form with the carbon some carbonic anhydride, and then some carbonic oxide, which reacts on the oxide of zinc. The carbonic anhydride, CO_2 , which is the product of this reaction, is again converted by the excess of carbon present into carbonic oxide. The carbonic anhydride yields double its volume of carbonic oxide; hence the accumulation of carbonic oxide is very rapidly effected, even though its production originated in only a "trace" of air, an important factor in the mechanism of reduction.

A state of equilibrium between the zinc oxide and carbonic anhydride does not become established, because carbonic anhydride is dissociated at the high temperature which exists.

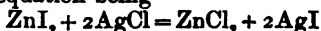
Oxide of lead heated with carbon gives only carbonic anhydride—in fact, the reaction $2\text{PbO} + \text{C} = 2\text{Pb} + \text{CO}_2$, is so slightly endothermic, that but little external aid is needed to change the conditions and render the reaction exothermic.

With regard to endothermic reactions generally, Victor Meyer gives a word of warning. He says*: "Decompositions accompanied by negative calorific effects, are more frequent at high

* *Modern Theories of Chemistry*, p. 442.

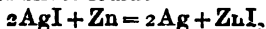
than at low temperatures. This fact is usually expressed by saying that the heat represents the work necessary for the decomposition of the compound, or yields the kinetic energy required, which in the decomposition is converted into potential energy. A fundamental difference between decompositions requiring a red heat and associated with a negative calorific effect, and those taking place at the ordinary temperature, does not exist; for in both cases the particles of the materials possess kinetic energy, a part of which, with consequent lowering of the temperature, is utilised in bringing about the decomposition. It is therefore at least inconsistent to regard decompositions of this kind taking place at high temperatures in a light different from quite analogous decompositions taking place at a lower temperature, and in fact to consider the former as abnormal, and to try by various artifices to explain them away. The fact to be recognised is that chemical changes requiring for their completion the aid of heat can take place under various conditions, and that such changes do take place more frequently, and the more easily the more heat there is to be disposed of, consequently at higher temperatures, but that such changes do not take place exclusively at high temperatures."

Decompositions associated with negative calorific effects take place usually very easily in association with others producing heat, so that in the total effect more heat is produced than is used. This may be well illustrated by a series of reactions on which an important metallurgical process (Claudet's) depends. Zinc iodide is used to separate silver from silver chloride, dissolved in brine, the equation being



$$60.6 \quad 2 \times 29 \quad 112.3 + 2 \times 14.3 = + 22.3$$

The expulsion of chlorine from silver by iodine in iodide of silver is quite in accordance with the fact that a greater amount of heat is liberated by the formation of chloride of zinc than silver chloride. In the second stage of the process, zinc again takes the iodine from iodide of silver, the heat of formation of zinc iodide being greater than that of silver iodide.



$$2 \times 14.3 \quad 60.6 = + 32$$

It is well to repeat that in the following equations the figures representing the thermal values are preceded by the plus or minus sign. This is a conventional mode of representation of the fact that heat has been gained or lost during the formation of the particular compound. In calculating the thermal value of any given set of reactions as represented by an equation, it is necessary to algebraically subtract the thermal value of all compounds

that are decomposed, and, conversely, to algebraically add the thermal values of the bodies formed.

The elements are assumed to be in the normal state of aggregation, unless it be otherwise stated, so that although an equation may be written $\text{CuS} + 3\text{O} = \text{CuO} + \text{SO}_2$, it must be understood that it is oxygen in its normal condition that is employed, and not nascent oxygen. The heats of aggregation are only known in a very few instances.

The heats of formation given in the following tables are mainly derived from the results found in the "*Annuaire du Bureau des Longitudes*." The numbers therein given have been adapted to agree with the chemical notation in use in this country. They are, it is believed, the most trustworthy that can be set before the student, and with their aid he will be able to obtain an insight into the thermal conditions which prevail when some of the

Heats of Formation of Some Gaseous Compounds.

Reaction.	Product.	Heat Evolved.	State of Product.
$\text{S} + 3\text{O}$	SO_2	+ 91.8	Gaseous.
"	SO_2	+ 103.6	Solid.
$\text{S} + 2\text{O}$	SO	+ 71.0	Gaseous.
$2\text{H} + \text{O}$	H_2O	+ 58.2	"
	H_2O	+ 69.0	Liquid.
$\text{C} + 2\text{O}$	CO_2	+ 97.0	Gaseous.
$\text{C} + \text{O}$	CO	+ 29.0	"
$2\text{H} + \text{S}$	SH_2	+ 4.6	"

principal metallurgical operations are being conducted. The thermal equations given on pages 305 will provide the student with a basis for such work. It will be observed that the synopsis of typical processes, page 312, contains reference numbers to these sets of distinctive thermal processes. It must, at the same time, be admitted that the basis for thermo-metallurgy is at present a somewhat slender one, as most of the data which have as yet been obtained are derived from "wet," and not "dry" reactions. It is well, therefore, to bear in mind the warning of Mendeléeff against "extracting exact consequences of importance to chemical mechanics" from the present store of thermo-chemical data. He points out* "that the majority of the determinations were conducted in weak aqueous solutions, and, the heat of the solution being known, were referred to the substances in solution." It must be remembered, however, it is probable that during both

* *The Principles of Chemistry*, vol. i. 1891, p. 171.

solution and dilution the water acts independently in a chemical sense on the substance dissolved, and that "physical and mechanical changes proceed side by side with chemical changes . . . and for the present it is impossible to distinguish the thermal effects of the one and of the other kind of change . . . purely chemical phenomena are inseparable from mechanical phenomena."

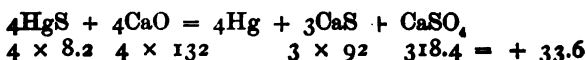
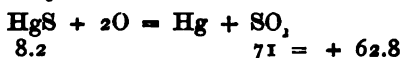
Heats of Change of the Isomeric Elements.

Name.	Heat Evolved.
Oxygen, changing to ozone (16 grammes) .	- 9.9
Sulphur, octahedral to insoluble variety .	0.0 at 18° < 0 at 112°
" insoluble amorphous to the soluble amorphous variety . . .	+ 0.08
" soluble amorphous to the octahedral . . .	- 0.08
" prismatic to octahedral . . .	+ 0.08
" plastic to octahedral . . .	+ 0.40
Selenium, vitreous to metallic variety .	+ 5.6
Tellurium, crystalline to amorphous variety	+ 24.2
Phosphorus, white to red crystalline variety	+ 19.2
" " " amorphous "	+ 20.7 + 9.3 and - i.e., according to the modification.
Arsenic, amorphous to crystalline variety	+ 1.1
Carbon, amorphous (charcoal) to diamond	+ 3.4
Silicon, amorphous to crystalline variety .	+ 8.1
Gold, precipitated from the bromide, to the physical state of gold precipitated from the chloride . . .	+ 3.2
Iron, about 700° (probably 650°) . . .	- 0.28
about 1000° (probably 850°) . . .	- 0.34

Thermal Equations for the Principal Metallurgical Operations.

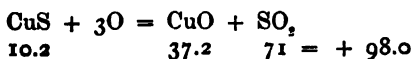
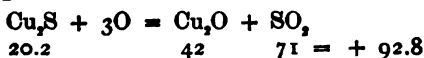
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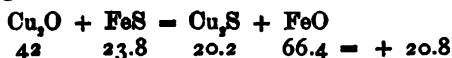
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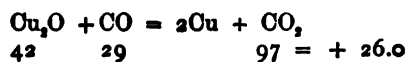
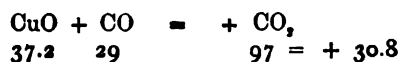
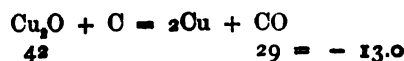
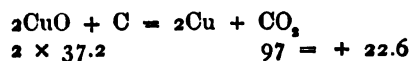
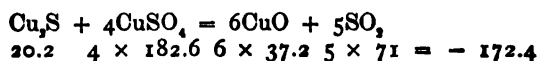
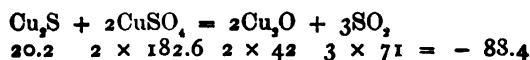
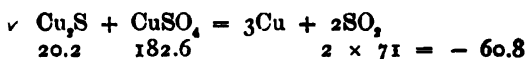
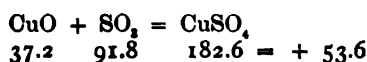
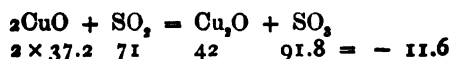
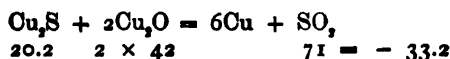
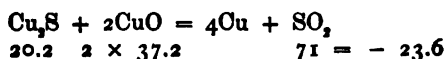
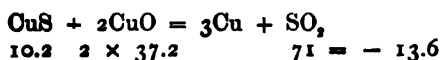
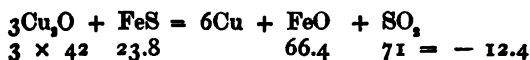
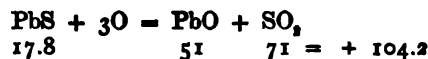
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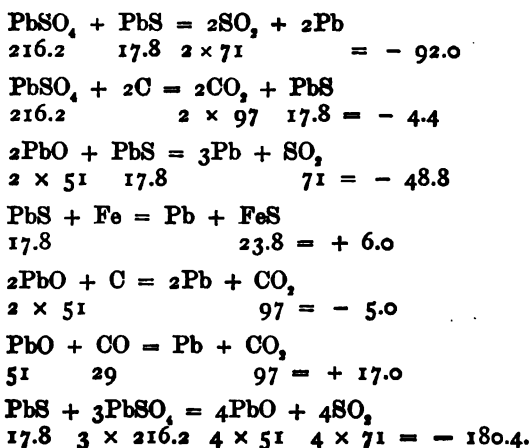
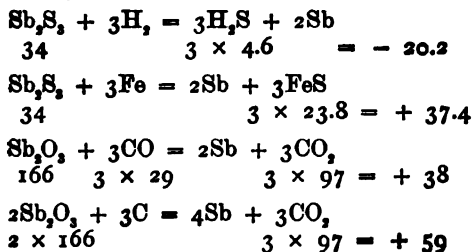
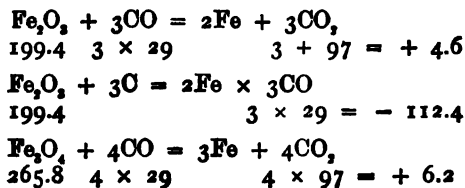
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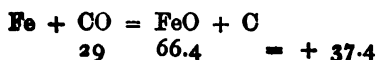
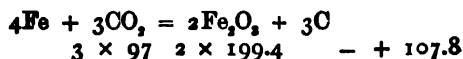
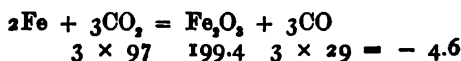
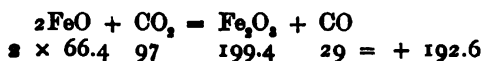
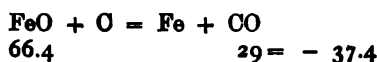
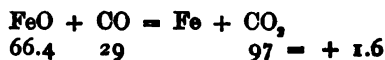
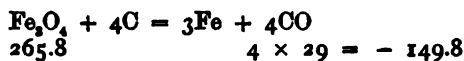
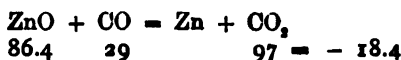
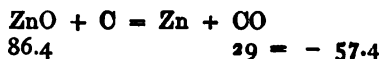
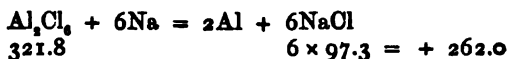
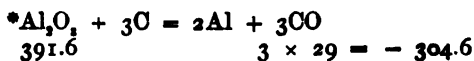
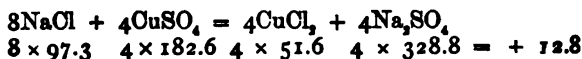


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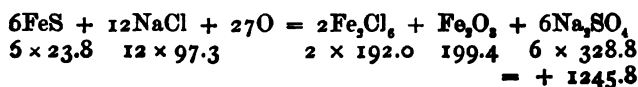
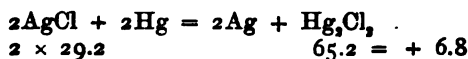
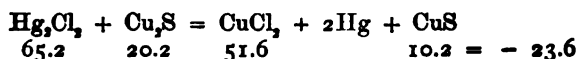
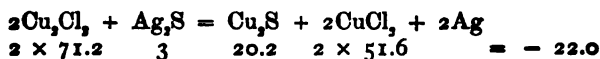
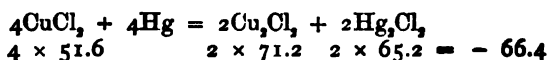
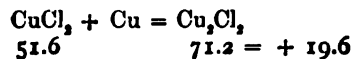
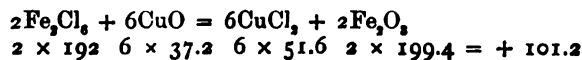
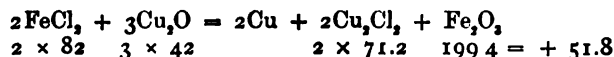
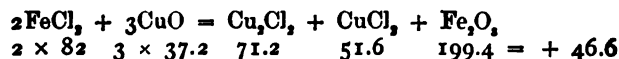
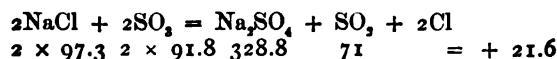
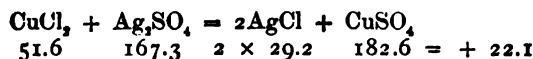
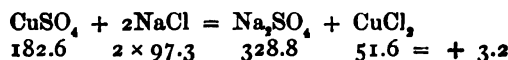
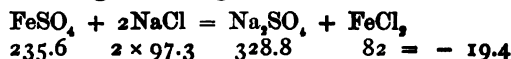
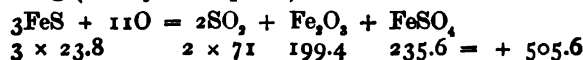
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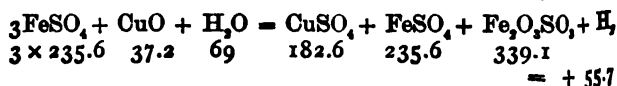
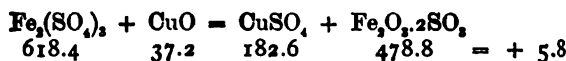
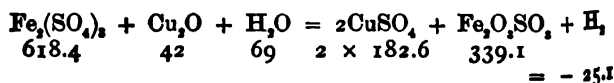
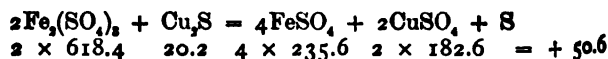
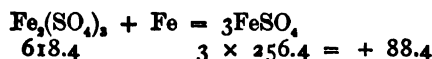
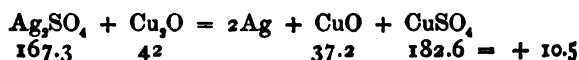
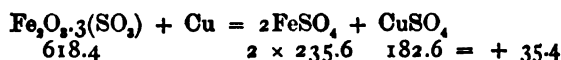
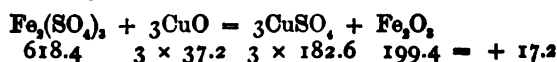
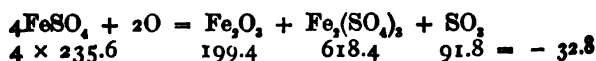
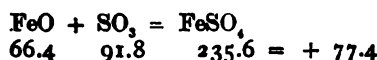
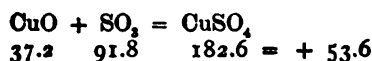
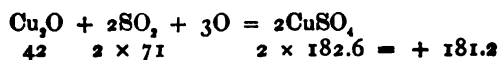
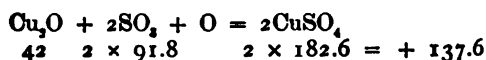
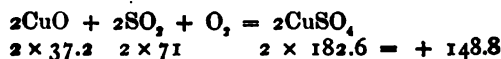
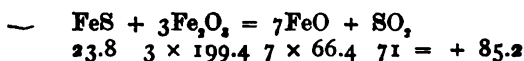
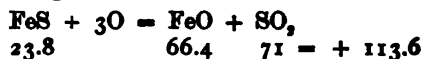
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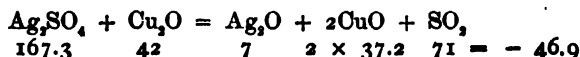
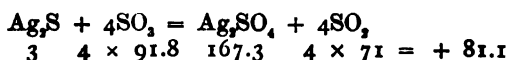
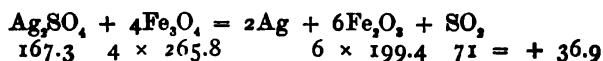
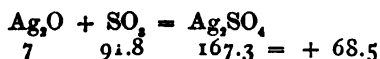
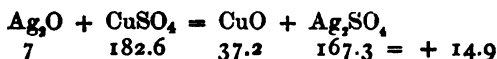
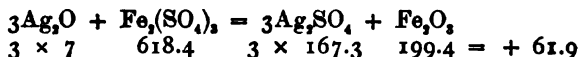
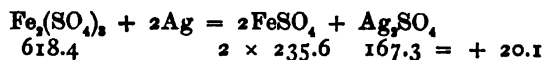
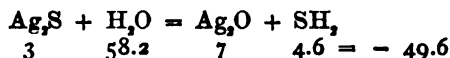
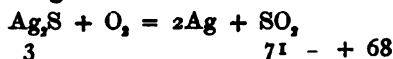
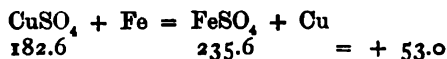
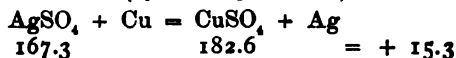
Lead—continued.**IV****Antimony.****V****Iron.**

Iron—continued.**VI****Zinc.****VII****Aluminium.****VIII****Silver.**

* Fremy, *Encyclopedie Chimique*. Paris. 1890.

Silver—continued.**IX****Chloridising Roasting.****X****Roasting (mainly to Sulphate).**

Roasting—continued.

Roasting—continued.**XI****Precipitation (by a cheaper metal).**

See also III and IV for cases of precipitation in the dry way of lead and antimony, from their sulphides, by iron.

The table given on the folding plate will enable the student to form other thermal equations for himself.

In calculating the heats of formation of the basic ferric sulphates, it has been necessary to assume that the heat evolved is proportional to the ratio of acid to base. It must be remembered that in the case of the combination of carbon and oxygen such a relationship does not exist.

BIBLIOGRAPHY.

- Berthelot.—"*Essai de Mécanique Chimique*," Paris, 1879; "*Traité Pratique de Calorimétrie Chimique*," Paris.
- H. le Chatelier.—"*Equilibres Chimiques*" (see "*Comptes Rendus*," vol. civ., 1888, pp. 355, 598, 1008).
- Prof. A. Ditte.—"*Leçons sur les Métaux*," Paris, 1891.
- P. Duhem.—"*Introduction à la Mécanique Chimique*," Paris, 1893.
- J. Willard Gibbs.—"*On the Equilibrium of Heterogeneous Substances*" (Trans. Connecticut Acad. vol. iii.).
- J. Moutier.—"*Sur quelques relations de la Physique et de la Chimie*" (Ency. Chimique de Fremy, Introduction, 1881).
- Muir & Wilson.—"*Principles of Thermal Chemistry*," London, 1885.
- A. Naumann.—"*Technisch-thermochemische Berechnung zur Heizung insbesondere mit gas förmigen Brennstoffen*, Braunschweig."
- W. Nernst.—"*Theoretische Chemie*," Stuttgart, 1893.
- Ostwald.—"*Lehrbuch der Allgemeinen Chemie*," Leipzig, 1893.
- J. Thomsen.—"*Thermochemische Untersuchungen*," Leipzig, 1882-3.
- J. J. Thomson.—"*On the Application of Dynamics to Physics and to Chemistry*," London (Macmillan), 1888.

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• Hydrogen, and Cyanogen.



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CHAPTER X.

TYPICAL METALLURGICAL PROCESSES.

Classification of Processes.—The methods that are adopted in extracting metals from their ores may conveniently be grouped in the following manner :—

The thick, black Roman Numerals refer to the Thermal Equations,
Chapter IX.

A. DRY PROCESSES.

I. a. *By Simple Fusion with Suitable Fluxes.*

- | | | |
|---|-------------------|--|
| (a) In blast or reverberatory furnaces. | 1. Gold . . . | { This process is only applicable to metals in an uncombined form. |
| | 2. Silver . . . | |
| | 3. Platinum . . . | |
| | 4. Copper . . . | |
| (b) In tube furnace. | 5. Bismuth . . . | By liqutation. |

β. *By Simple Heating.*

- | | | |
|----------------------------------|----------------------|--|
| (a) In kilns or reverberatories. | 1. Mercury (I) . . . | From its sulphide, the presence of air being necessary. |
| (b) In retorts. | 2. Arsenic . . . | From sulphides of arsenic and iron, air excluded, always with appliances for condensing the volatilised metal. |

II. *By Reduction of Oxide by Carbon.*

- | | | |
|---|----------------------------|---|
| (a) In blast furnaces or, more rarely, in hearths or crucibles. | 1. Copper (II) . . . | { Usually after previous roasting of sulphide or arsenide ; |
| | 2. Lead (III) . . . | |
| | 3. Antimony (IV) . . . | |
| | 4. Nickel . . . | |
| | 5. Iron (V) . . . | |
| (b) In reverberatory furnace. | 6. Nickel . . . | { Usually with simultaneous carburisation of the liberated metal. |
| | 7. Manganese . . . | |
| (c) In retort furnaces. | 8. Tin . . . | { Always after roasting the ore ; and with volatilisation of the liberated metal. |
| | 9. Bismuth . . . | |
| (d) In furnaces heated electrically. | 10. Zinc (VI) . . . | |
| | 11. Arsenic . . . | |
| | 12. Sodium . . . | |
| | 13. Aluminium (VII) . . . | |
| | 14. Calcium, Chromium, &c. | |

III. *By Concentration as Sulphide;*

usually followed by reaction between sulphide and oxide,
or between sulphide and sulphate.

(a) In reverberatory furnaces.	1. Copper(II). 2. Lead (III).	Usually after partial roasting; sometimes, in the case of lead and antimony, the removal of the sulphur and precipitation of the metals is aided by a cheaper metal, iron.
(b) In liquation furnace.	3. Antimony .	

IV. *By Concentration in Sulphide, or Arsenide, and subsequent smelting as in II. or III.*

In reverberatory or blast furnaces.	1. Gold. 2. Silver. 3. Nickel. 4. Cobalt.
-------------------------------------	--

V. *By Concentration in Other Metals, by Fusion.*

Usually in blast furnaces; but often in reverberatory furnaces.	1. Gold. 2. Silver. 3. Platinum.
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The metal is subsequently concentrated or extracted by (1) cupellation, (2) crystallisation (Pattinson process), (3) liquation, (4) recourse to wet methods, (5) superior affinity of a third metal (zinc in Parkes' process), (6) distillation (treatment of gold amalgam).

VI. *By Reduction of a Haloid Salt.*

In reverberatory furnaces or in crucibles.	1. Aluminium. { 2. Magnesium. {	The halogen is removed by sodium.
--	------------------------------------	-----------------------------------

B. PROCESSES INVOLVING THE USE OF MERCURY.

(a) In cradles, flumes, stamp batteries, concentrators . . .	1. Gold . . .	{ As part of the operation of dressing the ore.
(b) In pans and appliances of varied form . . .		
(a) In heaps . . .	2. Silver(VIII)	Patio process.
(b) In barrels . . .		Old Freiberg process.
(c) In copper-lined tubs . . .		Cazo process.
(d) In cast-iron pans . . .		Modern pan-amalgamation.

C. WET PROCESSES.

a. *Methods of Solution.*

These processes are usually conducted in earthenware vessels, or cast-iron pans, or wooden vats, usually lined.

I. *a. Solution in Acids.*

- | | |
|-----------------|---|
| 1. Gold . . | In aqua regia. |
| 2. Platinum . . | Ditto. |
| 3. Silver . . | In nitric or sulphuric acid. |
| 4. Bismuth . . | In hydrochloric acid. |
| 5. Nickel . . | The oxides, obtained by
roasting sulphides or arsenides,
are dissolved usually in hydro-
chloric acid. |
| 6. Cobalt . . | |
| 7. Zinc . . | |
| 8. Copper . . | |
| 9. Lead . . | |

b. *Solution in Alkaline Salts.*

- | | |
|---------------|-----------------------|
| 1. Gold . . | In potassium cyanide. |
| 2. Silver . . | In hyposulphites. |

II. *Roasting to Sulphate, and extracting with Water.*

- | | |
|-----------------|------------------------------------|
| 1. Silver .(X). | (Ziervogel process.) |
| 2. Copper (II). | The metal is precipitated by iron. |

III. *Roasting with Salt, Soluble Chloride being formed.*

- | | |
|------------------|--------------------------------------|
| 1. Silver .(IX). | (Augustin and Von Patern processes.) |
| 2. Copper . . | (Longmaid and other processes.) |

IV. *Formation of Soluble Chloride by Gaseous Chlorine.*

- | | |
|---------------|---|
| 1. Gold . . | Plattner's process and its modifications. In some cases, chlorine is replaced by bromine, a soluble bromide being formed. |
| 2. Silver . . | Any silver chloride, formed in the treatment of gold, may be dissolved out by sodium hyposulphite or brine. |

B. *Methods of Precipitation.*

- | | |
|-----------------|---|
| 1. Silver . | Replacement by a cheaper metal. |
| 2. Copper (XI). | |
| 1. Gold . . | By a precipitating agent. |
| 2. Platinum . . | |
| 1. Bismuth . . | By precipitation, followed by reduction in the dry way. |
| 2. Nickel . . | |
| 3. Cobalt . . | |
| 4. Zinc . . | |
| 5. Lead . . | |

D. ELECTROLYTIC METHODS.

At the present time, electrolysis is mainly employed in the refining of copper. Numerous electrolytic methods of extracting

metals from their ores have frequently been brought forward; few, however, have advanced beyond the experimental stage.

1. Copper . . . From blister-copper or regulus.
2. Lead . . . Keith's process.
3. Gold . . . By nascent chlorine produced electrolytically.
4. Aluminium . . . From aluminium in its fused salts.
5. Antimony . . . Borchers' process.*

It is impossible in a work of this description to deal fully with the methods that are adopted in extracting even the principal metals from their ores, nor is it desirable to attempt to do this, for the student has an abundant technical literature at his disposal. It is far more important that at the outset of his work he should make himself familiar with the nature of metallurgical operations generally, so that he may see in what points they differ from those conducted either in the laboratory or in purely chemical works. With this object in view, a few typical metallurgical processes have been chosen for somewhat full treatment, care having been taken to select those which present considerable complexity of detail, since a knowledge of such groups of processes as those adopted in industrial centres like Swansea, Denver, and Freiberg gives the student a clearer insight into the practice of metallurgy than desultory reading affords.

Welsh Method of Copper-smelting.—This method, in modified forms, conducted in reverberatory furnaces, is employed for a large proportion of the world's production of copper. In Germany a blast-furnace method is employed. The one broad distinction between this method and the Welsh method consists in the fact that in the latter copper sulphide is the reducing agent, whilst in the German process it is carbonic oxide. Both processes depend essentially on the affinity which copper has for sulphur, which enables it to form a regulus while the associated metals are eliminated in an oxidised form.

In the Welsh method (Fig. 78) comparatively poor ores, consisting of copper pyrites with a considerable proportion of iron pyrites, containing 5 to 15 per cent. of copper, richer ores of the same composition containing 15 to 25 per cent. of copper, and copper pyrites with oxidised ores, are mixed so as to contain 9 to 15 per cent. of copper. The smelting method varies with

* *Dingler's Polytechnisches Journal*, vol. cclxvi. (1887), p. 283. On electrolytic methods consult Balling, *Die Electro-Metallurgie*.

WELSH PROCESS OF COPPER SMELTING.

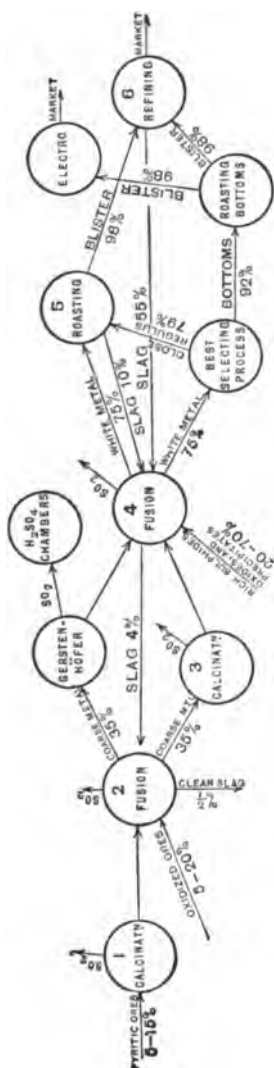


FIG. 78.

the nature of the ore, but it usually comprises six distinct processes:—

1. *Calcination of Mixed Ores.*

—This consists in roasting the pyritic ores, whether rich or poor, containing iron pyrites, arsenic, and antimony. The roasting is always incomplete, and the extent to which it is carried depends on the proportion of sulphides available for the subsequent operations.

2. *Fusion of the Roasted Ores for Regul.*

—The ores are fused with slag rich in cuprous oxide, known as *metal-slag*, from the fourth operation. Fluorspar is useful as a flux, and is added with oxides and carbonates. The operation gives two products—a regulus, *coarse-metal*, in which it has been attempted to concentrate all the copper, and a slag, *ore-furnace slag* which seldom contains more than 0.5 per cent. of copper and is mostly thrown away. The regulus contains 30 to 34 per cent. of copper and 23 per cent. of sulphur. It also contains a notable quantity of arsenic, antimony, and tin.

3. *Calcination of Coarse-metal.*

—This calcination is always incomplete, but its degree of perfection depends on the quantity of oxidised ores which it is possible to reserve for the subsequent operation.

4. *Fusion of Calcined Coarse-metal.*—In this operation roasted regulus and sulphuretted ore rich in copper, and containing

but little sulphide of iron, are employed. Oxidised ores of copper, free from arsenic, antimony, and tin, are also added. Two products are obtained, regulus, containing 65 to 80 per cent. of copper, and 18 to 22 per cent. of sulphur. The slag, *metal-slag*, is a ferrous silicate, containing a little oxide of copper and shots of metallic copper, the total amount of copper it contains being 2 to 3 per cent. This slag is melted in operation 2.

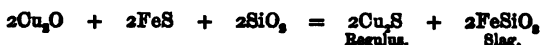
5. *Roasting the Regulus*.—This operation is very complex, and comprises a series of fusions and roastings in an oxidising atmosphere. Its object is to purify the regulus and to scorify the iron, and to bring as much as possible of the copper to the metallic state. To operations of this character the Welsh smelter applies the term *roasting*, as distinguished from *calcining*. Two products are obtained, *blister-copper*, containing about 98 per cent. of copper, and a slag, *roaster-slag*, which always contains oxide of copper, shots of metallic copper, and often a small proportion of arsenic, antimony, and tin. This slag is usually added to the charge in operation 4.

6. *Refining and Toughening*.—The object of this operation is to purify the copper by oxidising the foreign bodies that it contains. The refining should bring the metal to the malleable state of *marketable* copper. The slag obtained, *refinery-slag*, is very rich in copper, about 55 per cent., and is added to the charge in operation 4.

In the Welsh method of copper smelting, reverberatory furnaces are exclusively employed, the area of the grate being generally about one-fifth of that of the hearth. The furnaces used for calcination have very deep fireplaces, so as to give reducing gases; but they have an abundant supply of oxygen from the air, which is admitted through holes in the fire-bridge. The ore is charged-in through a flat hopper, in which it is allowed to dry for some time before being introduced into the furnace. The internal dimensions of the calcining furnaces are usually 30 feet by 12 feet, or 21 feet by 12 feet. The charge is 3 to 6 tons of ore, the calcination occupying 12 to 24 hours. The doors are then closed, and the temperature raised in order to decompose the sulphates. The gas evolved may consist of 10.6 per cent. of sulphurous and carbonic anhydrides, 9 per cent. of oxygen, and 80 per cent. of nitrogen.

The furnaces, in which the fusion for regulus is effected, are so arranged as to give a high temperature, and the fireplace is consequently large in comparison with the laboratory portion. The bed consists of a series of layers of compressed sand cemented

with metal-slag. It is about 15 to 20 inches in thickness, and slopes in all directions towards a tap-hole. There is a door in proximity to the flue, and through this door the slag is skimmed without allowing the air to pass over the regulus and oxidise it. In front of the tap-hole is a perforated receptacle, which can be lowered by a crane into a tank full of water. The bed is about 14 feet long, the distance between the top of the bridge and the roof being 23 inches. The charge is usually 2 tons of ore. Slags from subsequent operations are added, and fluorspar, if much earthy gangue is present. The materials used in this first fusion for regulus are chiefly oxides and sulphides of copper and iron, and the operation consists essentially in obtaining copper sulphide, thus :—



The sulphides must be in excess, otherwise copper will be absorbed in the slags, and copper will be obtained.

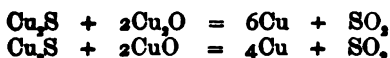
The calcination* of the regulus is effected in a furnace similar to that used for the first calcination. The charge is $3\frac{1}{2}$ to $6\frac{1}{2}$ tons of regulus. The reactions taking place are similar to those in the first calcination. The process occupies twenty to thirty-six hours, and 12 per cent. of the sulphur is eliminated.

The second fusion is conducted in a similar manner to the first fusion for coarse-metal. The charge is 2 tons of calcined coarse-metal and 12 cwt. of slag and oxidised ores. The regulus obtained consists of white-metal (75 per cent. of copper), or blue-metal (60 per cent. of copper), or pimple-metal (81 per cent. of copper). The slag is a silicate of iron, with about 4 per cent. of copper. The reactions are similar to those that obtain in the first fusion for regulus. Blue-metal contains some sulphide of iron, and pimple-metal contains an excess of the oxidised copper compounds. When very impure ores are dealt with, it is often found advisable to allow a little coarse copper to form as bottoms.

The roasting of these different varieties of regulus is conducted in a reverberatory furnace with a deep hearth. The process is prolonged as much as possible, and thus the arsenic and antimony may be caused to escape before the actual reducing action commences. When the pasty mass has collected at the bottom of the furnace the temperature is raised, and the reaction between

* Copper smelters call these operations *calcination*, but *roasting* would be more accurate.

the sulphide and the oxide takes place, metallic copper being formed. The chief reactions may be expressed thus—



This impure copper, blister-copper, is refined in furnaces similar to those used for fusion, except that the bed is deeper and the fireplace larger. The charge consists of about 10 tons of blister-copper in the form of pigs, which are loosely stacked, and an abundant supply of air is provided, so as to oxidise the metal as much as possible. The temperature is raised gently to the melting-point of copper; it is then moderated in order that the fusion may be prolonged and oxidation occur. The melting occupies five to six hours, and the moderate heating is continued for five to six hours more, in order that the iron, antimony, arsenic, &c., may be completely oxidised. The temperature is then raised much higher for three to four hours more, when the oxidised products form a thin slag, containing a considerable quantity of copper oxide. This is raked off, and the surface covered with a layer of the purest anthracite or charcoal. A long pole of wood, green wood by preference, is pushed beneath the surface of the molten metal and held down by a suitable metal bar. The violent evolution of gas from the wood causes the metal to splash up amongst the carbonaceous covering, and this, with the gases from the wood, reduces, to the metallic state, the copper oxide that exists dissolved in the copper to the extent of 4 per cent. A small amount of the oxide must be left, and the workman judges, from a sample that he takes from time to time and tests by breaking in a vice, whether it is still "dry" or at "tough-pitch," that is, ready for market, or "overpoled." If the last, he removes the carbon covering, and exposes the metal to the action of the air.*

Smelting of Gold and Silver Ores in Colorado.—The old works of the Boston and Colorado Smelting Company at Black Hawk have disappeared, and the modification of the Swansea system adopted, which was fully described by Dr. Egleston † in 1875, has been so far changed in the method now practised at

* Fuller information on the Welsh method of copper smelting will be found in the following works:—Percy, *Metallurgy*, vol. i. (London, 1861), p. 314; Vivian, *Copper Smelting: Its History and Processes*, 1881; Howe, *Copper Smelting*, Washington, 1885; Le Play, *Procédés Métallurgiques employés dans le Pays de Galles*, Paris, 1848; Rivot, *Principes généraux du Traitement des Minéraux métalliques*, Paris, 1871.

† *Trans. Amer. Inst. Min. E.*, vol. iv., 1875, p. 276.

the Argo works, near Denver, as to be scarcely recognisable, excepting so far as the general principles are involved. The following is a short sketch, borrowed from Mr. R. Pearce's Presidential Address, delivered at the meeting of the American Institute of Mining Engineers, in June 1889.

About 200 tons of ore is smelted per day, the ores including a great variety of copper, silver, and gold ores from Colorado, as well as from other Western States and Territories, and averaging 40 to 60 oz. of silver and $\frac{1}{2}$ to 1 oz. of gold per ton, and 2 to 3 per cent. of copper. About 90 per cent. of the ore contains no copper, the other 10 per cent. furnishing that metal in sufficient quantity to make up the general average to 2 to 3 per cent. Half the ore, 100 tons per day, is roasted in furnaces or in kilns, but the operation is not complete in either case, as sulphur is always allowed to remain to the extent of 5 to 7 per cent. The other 100 tons are smelted without roasting. The roasted ore and siliceous ores are mixed so as to yield a slag containing 40 per cent. of silica and a regulus (ore metal) containing 40 per cent. of copper and 400 oz. of silver and 6 oz. of gold per ton. The capacity of each furnace is about 25 tons of ore per day, with 2 tons of rich slags added from other operations. In this smelting 13 tons charged yield 1 ton of ore-metal. This regulus always contains a certain amount of lead, but the proportion rarely exceeds 10 per cent.

In the next stage of the process, the charge consists of a mixture of two-thirds of roasted ore-metal and one-third of unroasted ore-metal, together with rich siliceous silver ore, in quantities sufficient to prevent corrosion of the furnace by the iron in the regulus. The concentration-furnace in which this operation is effected stands 3 feet above the level of the ore-furnace, so that the rich slag from the former may, when skimmed, flow directly into the latter, where it is reduced to the condition of ordinary ore-furnace slag. This effects a great saving in the cost of re-smelting these rich slags. The regulus obtained contains 700 to 800 oz. of silver and 10 oz. of gold per ton, together with 60 per cent. of copper, each ton representing 20 to 21 tons of ore. This regulus is now ready for the extraction of the silver, which comprises the following operations:—

Rough roasting.

Fine grinding.

Fine roasting for silver sulphate.

Lixiviation, and the precipitation of the silver.

Refining and melting of the cement silver.

x

The regulus is then crushed so as to pass through a screen of 6 meshes to the inch, and roasted for twenty-four hours. The bulk of the sulphur is driven off, and oxide of copper is formed, the mass still containing sufficient sulphur for the subsequent operation of roasting for silver sulphate. After cooling, the roasted material is ground fine under edge-rollers and passed through a 60-mesh screen. It is then ready for fine roasting or conversion of the sulphide into a sulphate.

This operation, based on principles pointed out by Ziervogel, lasts about five hours. The first stage is conducted at a low temperature, and lasts about an hour and a half, copper sulphide being oxidised with evolution of heat. In the second stage, at a slightly increased temperature for an hour and a half, the material increases in volume, and assumes a porous appearance from the formation of copper sulphate. In the third stage, the temperature is further increased for an hour or until the silver is completely changed into sulphate. If cuprous oxide is present at this stage, it will, during the operation of lixiviation with water, cause the reduction of the silver sulphate to metallic silver. The charge is consequently vigorously stirred, and turned over, in the fourth and last stage, in order to completely oxidise any cuprous oxide. The results of the operation are very materially affected by arsenic, by antimony, and, above all, by bismuth, metals which form insoluble silver compounds. The lixiviation of the roasted regulus is effected in tubs, and nothing but hot water is required. The solution, charged with silver sulphate, is allowed to flow over copper plates for the precipitation of the silver, a process requiring but little attention. The solution enters tank No. 1, charged with silver, and leaves tank No. 2, charged with copper, and without a trace of silver. It finally flows over scrap iron for the precipitation of the copper. In the precipitated silver, some copper is found in the form of cuprous oxide or as metal. This is removed by prolonged boiling with water containing a small quantity of sulphuric acid, into which air is injected by a small steam-jet. The copper sulphate formed is carefully washed out of the silver, which is then dried and melted into bars of an average fineness of 999.

The residues from the silver extraction contain about 40 oz. of silver and 10 oz. of gold per ton, and 65 per cent. of copper as cupric oxide. They also contain lead and bismuth as sulphates and iron as ferric oxide. They are mixed with pyritic ores containing gold, pyrites rich in sulphur and poor in silver, and siliceous gold ores, and are smelted direct for regulus with 65 per

cent. of copper, and 10 to 15 oz. of gold and 80 oz. of silver per ton. The slag, which is similar in composition to that from the ore-furnace, is thrown away.

This regulus is treated so as to obtain a rich copper-gold alloy. This process involves two operations—(1) a combined roasting and smelting, and (2) a refining of the crude alloy. The aim of the process is to concentrate the gold contained in the regulus into a rich gold-silver-copper alloy, containing also the bulk of the impurities existing in the regulus. This process is similar to the Swansea method of making "best selected copper." At Argo, about 12 tons of slabs of regulus, residue metal, are placed on the hearth of a large reverberatory furnace, and melted after partial oxidation. In the last stage of the melting, a reaction takes place between the oxide and sulphide, and a certain amount of metallic copper is liberated. This contains nearly all the gold, together with any foreign metals present in the regulus. The charge is tapped into sand-moulds, and the first few pigs nearest the tap-hole are found to have, under the enriched regulus, plates of this impure copper, commonly known as metallic bottoms. The proportion of these to the whole tap of regulus, or pimple-metal, is about 1 to 15. The bottoms contain 100 to 200 oz. of gold to the ton, and about 300 oz. of silver. They are subjected to processes of refining and separation, whereby the gold is recovered.

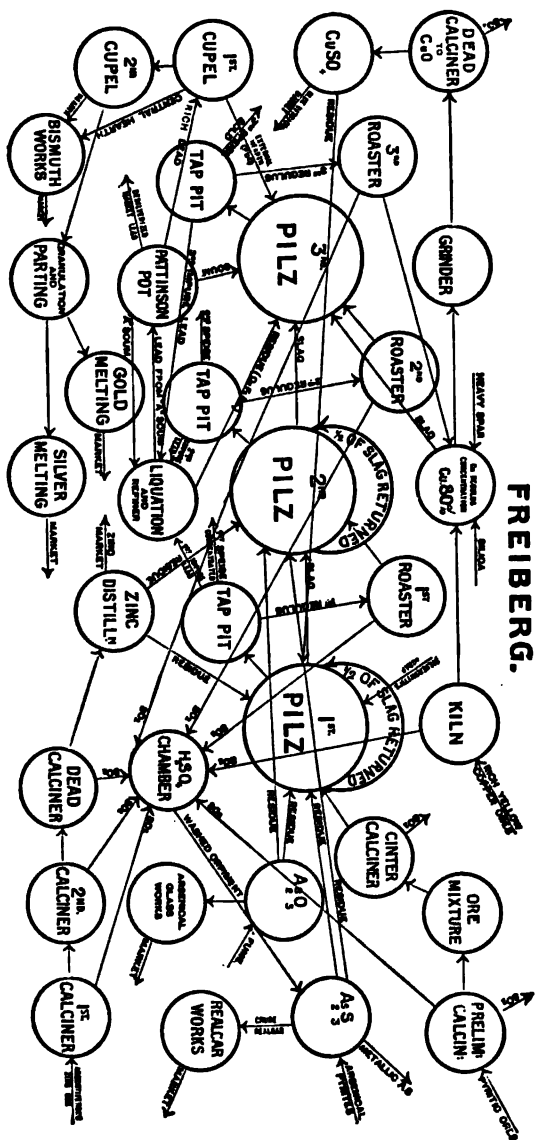
The pimple-metal, if the operation has been properly conducted, contains 0.1 to 0.2 oz. of gold per ton, 90 oz. of silver, and 77 per cent. of copper. It is crushed, roasted, ground fine, and again roasted to form silver sulphate. In fact, it is treated by the Ziervogel process in precisely the same manner as the rich silver regulus; but, as it contains no gold, a separate set of furnaces is used. The residue consists almost entirely of copper oxide with less than 10 oz. of silver per ton. It is dried, packed in barrels, and sold to the manufacturers of sulphate of copper, or is reduced to black copper by melting with small coal slack in a reverberatory furnace.

Freiberg Process.—The smelting works at Freiberg,* in Saxony, were originally established to treat the ores obtained from the mines of the district. At the present time, ores from all parts of the world are also smelted. There are also two works, of which

* Descriptions of the various operations conducted in these works will be found in the following books:—*Freibergs Berg- und Hüttenwesen*, Freiberg, 1883; *Festschrift zum hundertjähr. Jubiläum der k. Bergakademie zu Freiberg*, Dresden, 1866; Percy, *Lead*, p. 303, *Silver and Gold*, p. 543; *Arche, Die Gewinnung der Metalle*, part i., 1888.

the more important is situated about three miles from the town of Freiberg, the other being somewhat more distant.

The ores treated consist chiefly of the sulphides of lead; but silver and copper are always present in the mixture of ores which constitutes the furnace-charge. The plant also includes furnaces for the treatment of ores of zinc, arsenic and antimony fume. As an incidental process, sulphuric acid is made both by the ordinary lead-chamber method, and by a process in which the gases containing the sulphurous anhydride are stated to be passed over perforated clay slabs covered with platinised asbestos. Bismuth is also extracted from the portions of the cupellation hearths in which is collected the greater part of the bismuth that was originally contained in the lead treated. Provision is also made for the extraction of copper, nickel, and cobalt present in the ores. The relation borne by the respective sections to each other and to the general plan of operations is indicated by the accompanying diagrammatic scheme (Fig. 79). The various departments of the work are kept distinct, and the treatment, as a whole, centres round the smelting of the lead ores, the various residues from the treatment of other ores, frequently rich in the precious metals, being added to the lead-smelting charge. It is in this latter treatment that the distinctive features of the Freiberg smelting-process are found, the lead ores being smelted in admixture with the copper ores and argentiferous and auriferous residues. For this purpose the Pilz water-jacketed furnaces (Fig. 64) are used. They were originally introduced about the year 1865 to replace the older types of blast-furnace which had long been employed. The extraction of silver by the classical Freiberg amalgamation process, conducted in barrels, was also abandoned about this period, and was replaced by the method still in use, by which the precious metals are collected in the smelted lead. The main features of this process are as follows:—In order to impart the necessary degree of strength and coherence to enable them to be treated in the blast-furnace, as well as to obtain them in pieces of a size adapted to such treatment, the ores are first roasted at a temperature sufficiently high to clot the mass. This is effected by subjecting a suitable mixture of ores to an oxidising roasting in a long-bedded reverberatory furnace. The sulphur of the ore is in this way oxidised, and the metals are left chiefly in the form of oxides. Towards the end of the roasting the temperature of the furnace is raised to a degree sufficient to partly fuse the oxidised charge then present; the roasted material can in this state be withdrawn from the furnace into sheet-iron wheel-barrows, in which it is allowed to solidify. The



but little sulphide of iron, are employed. Oxidised ores of copper, free from arsenic, antimony, and tin, are also added. Two products are obtained, regulus, containing 65 to 80 per cent. of copper, and 18 to 22 per cent. of sulphur. The slag, *metal-slag*, is a ferrous silicate, containing a little oxide of copper and shots of metallic copper, the total amount of copper it contains being 2 to 3 per cent. This slag is melted in operation 2.

5. *Roasting the Regulus*.—This operation is very complex, and comprises a series of fusions and roastings in an oxidising atmosphere. Its object is to purify the regulus and to scorify the iron, and to bring as much as possible of the copper to the metallic state. To operations of this character the Welsh smelter applies the term *roasting*, as distinguished from *calcining*. Two products are obtained, *blister-copper*, containing about 98 per cent. of copper, and a slag, *roaster-slag*, which always contains oxide of copper, shots of metallic copper, and often a small proportion of arsenic, antimony, and tin. This slag is usually added to the charge in operation 4.

6. *Refining and Toughening*.—The object of this operation is to purify the copper by oxidising the foreign bodies that it contains. The refining should bring the metal to the malleable state of *marketable* copper. The slag obtained, *refinery-slag*, is very rich in copper, about 55 per cent., and is added to the charge in operation 4.

In the Welsh method of copper smelting, reverberatory furnaces are exclusively employed, the area of the grate being generally about one-fifth of that of the hearth. The furnaces used for calcination have very deep fireplaces, so as to give reducing gases; but they have an abundant supply of oxygen from the air, which is admitted through holes in the fire-bridge. The ore is charged-in through a flat hopper, in which it is allowed to dry for some time before being introduced into the furnace. The internal dimensions of the calcining furnaces are usually 30 feet by 12 feet, or 21 feet by 12 feet. The charge is 3 to 6 tons of ore, the calcination occupying 12 to 24 hours. The doors are then closed, and the temperature raised in order to decompose the sulphates. The gas evolved may consist of 10.6 per cent. of sulphurous and carbonic anhydrides, 9 per cent. of oxygen, and 80 per cent. of nitrogen.

The furnaces, in which the fusion for regulus is effected, are so arranged as to give a high temperature, and the fireplace is consequently large in comparison with the laboratory portion. The bed consists of a series of layers of compressed sand cemented

with metal-slag. It is about 15 to 20 inches in thickness, and slopes in all directions towards a tap-hole. There is a door in proximity to the flue, and through this door the slag is skimmed without allowing the air to pass over the regulus and oxidise it. In front of the tap-hole is a perforated receptacle, which can be lowered by a crane into a tank full of water. The bed is about 14 feet long, the distance between the top of the bridge and the roof being 23 inches. The charge is usually 2 tons of ore. Slags from subsequent operations are added, and fluorspar, if much earthy gangue is present. The materials used in this first fusion for regulus are chiefly oxides and sulphides of copper and iron, and the operation consists essentially in obtaining copper sulphide, thus:—



The sulphides must be in excess, otherwise copper will be absorbed in the slags, and copper will be obtained.

The calcination* of the regulus is effected in a furnace similar to that used for the first calcination. The charge is $3\frac{1}{2}$ to $6\frac{1}{2}$ tons of regulus. The reactions taking place are similar to those in the first calcination. The process occupies twenty to thirty-six hours, and 12 per cent. of the sulphur is eliminated.

The second fusion is conducted in a similar manner to the first fusion for coarse-metal. The charge is 2 tons of calcined coarse-metal and 12 cwt. of slag and oxidised ores. The regulus obtained consists of white-metal (75 per cent. of copper), or blue-metal (60 per cent. of copper), or pimple-metal (81 per cent. of copper). The slag is a silicate of iron, with about 4 per cent. of copper. The reactions are similar to those that obtain in the first fusion for regulus. Blue-metal contains some sulphide of iron, and pimple-metal contains an excess of the oxidised copper compounds. When very impure ores are dealt with, it is often found advisable to allow a little coarse copper to form as bottoms.

The roasting of these different varieties of regulus is conducted in a reverberatory furnace with a deep hearth. The process is prolonged as much as possible, and thus the arsenic and antimony may be caused to escape before the actual reducing action commences. When the pasty mass has collected at the bottom of the furnace the temperature is raised, and the reaction between

* Copper smelters call these operations *calcination*, but *roasting* would be more accurate.

cent. of the precious metals. This requires a higher temperature for its further treatment, and it is therefore removed from the large furnace to a similar but much smaller one, in which the remaining portion of the lead is eliminated, the fused gold and silver being granulated by pouring into water, the granules dried, and the gold and silver parted by the aid of sulphuric acid.

The litharge, if of a yellow colour, is reduced to the metallic state by a reducing-fusion in a small Pilz furnace, but any red litharge that is produced is sold as such. The beds of both the large and the small cupellation-furnaces show green spots at the places where the final products, rich in gold and silver, collected; the bismuth, not being removed by oxidation until nearly all the lead has been oxidised, passes into these portions of the marl-beds, colouring them green. These green patches are carefully removed, dissolved in hydrochloric acid, and the bismuth oxychloride is precipitated by dilution with water. This is either sold as such after purification, or else is reduced to the metallic state by fusion in crucibles with iron. The other portions of the marl cupellation beds, being rich in lead, are on this account added to the various smelting-charges.

Zinc.—The argentiferous zinc ores are roasted, the sulphurous anhydride evolved being collected and converted into sulphuric acid. The desulphurised ore is then mixed with charcoal, and placed in the retorts, which are heated in a regenerative furnace by gaseous fuel. The zinc distils over, and is collected in fire-clay receivers, and, after refining in a special reverberatory furnace, is sent to market. The residues left in the retorts contain the precious metals, and are charged into the Pilz furnaces with the lead-ores.

The zinc rich in silver and gold obtained by the Parkes process is distilled in an ordinary Morgan furnace, which consists of a hooded crucible contained in a wind-furnace. This completes the lead-smelting process proper, both the gold and silver present in the original materials treated having been collected, and the desilverised lead obtained in a form in which it is ready for the market.

The *cupriferous regulus* resulting from the ore-smelting contains usually but a few per cent. of copper, and consists chiefly of the sulphides of iron and lead. It may be mentioned that it is necessary to have considerable quantities of iron present in the furnace-charge, partly on account of the desulphurising action of the reduced metal, and partly because considerable quantities of zinc are usually present, and the zinc-oxide, passing into the slag,

would render it exceedingly pasty and difficult to fuse, were it not for the counteracting influence of large quantities of ferrous oxide.

This regulus, if its composition is such that this treatment is admissible, is roasted in kilns, the sulphurous anhydride produced being utilised in the manufacture of sulphuric acid. When roasted the regulus is added to the slag-smelting charge; the greater portion of the lead-oxide contained in the roasted regulus is then reduced to the metallic state, and a second regulus is produced, which is poorer in lead but richer in copper than was the one resulting from the ore-smelting. This regulus is too rich in copper to admit of its being roasted in kilns, the tendency of the pieces of regulus to clot together during the roasting being too great; it is therefore roasted in "stalls" which are built of brick, and much resemble ordinary cattle-stalls; they are roofless, with low surrounding walls and a slightly sloping bed. On this bed wood is placed, the regulus to be roasted being piled up on it, and then covered over with a compact layer of finely divided roasted pyrites or regulus. The stalls are placed in rows side by side, and back to back, a tunnel being left between every two such rows. Into this tunnel the gases resulting from the roasting are drawn through perforations in the back walls of the stalls, and are led away to the sulphuric-acid chambers. The combustion is started by lighting a small fire in a grate outside the stall; this kindles the wood, the heat evolved by the combustion of the sulphur in the regulus being afterwards sufficient to continue the process without the addition of any other fuel. This roasted second regulus is then treated as before, until a regulus is produced which contains about 35 per cent. of copper.

Instead of this repeated roasting and treatment with the slag-charge, the regulus, after having been roasted, may be treated in a cupola, together with lead-slugs and other fluxing and reducing additions. The product is a comparatively rich regulus, the lead originally present being reduced to the metallic state, taking with it the silver, the enriched regulus retaining but little of the precious metals. When enriched to the degree mentioned above, the regulus is brought, by a single roasting in an ordinary Welsh reverberatory furnace, to a "white" or "pimple" metal containing about 75 to 80 per cent. of copper. This is not further treated at the Muldenhütte, the principal works at Freiberg, but is sent to the Halsbrücke works, where it is roasted sweet, and the copper converted into copper sulphate by treating the roasted material with sulphuric acid. Any lead and gold that

may have been present remain undissolved, as does also the greater portion of the silver, the small quantity that passes into solution being reprecipitated by metallic copper. The undissolved lead residue is added to the blast-furnace treatment.

Speise.—This is a comparatively rare product. The nickel and cobalt it contains are concentrated by a process resembling that for the concentration of the copper in the regulus, the speise being first roasted and then re-melted with fluxes, such as lead-slugs, and with reducing agents, in a small blast furnace. Metallic lead is obtained, which contains the greater portion of the precious metals originally present in the speise, and the latter is much richer in nickel and cobalt after this treatment than it was before. In this concentrated state it is sold to outside works, where it is treated by the wet process, the residues, which contain the gold and silver of the speise, being bought back by the Government works.

The *ore-slag* is treated in the manner that has been described, the resulting slag, poor in lead, being thrown away. This contains about $2\frac{1}{2}$ per cent. of lead and 0.0045 per cent. of silver, the zinc-oxide also present occasionally reaching some 20 per cent.

The *fume* contains large quantities of lead-oxide, together with zinc-oxide and arsenious anhydride, which is collected and sold after a further sublimation. The oxides of lead and zinc remain on the bed of the furnace, and are added to the blast-furnace charge.

Thus, the general scheme of treatment is as follows :—The ores are mainly those of lead, copper, zinc, and silver. The products are, lead, zinc, bismuth, silver, gold, arsenic, as metals, and copper, mainly recovered as sulphate. Besides these, there are also incidental products, such as sulphate of iron and sulphate of manganese. Nickel and cobalt are recovered as arsenides—that is, in the form of speise; and the arsenic is recovered partly as metal, but mainly as powdery arsenious anhydride, and as red, yellow, and white arsenical glass.

The ores come partly from surrounding mines, and partly from foreign sources, the latter being smelted mainly for the copper, silver, and gold they contain. Almost all the ores are argentiferous. The principal portion of each charge consists of lead-ores, and these are divided into galenas with 30 per cent. or more of lead, and poor lead ores with 15 to 20 per cent. In the mean they contain generally 40 per cent. of lead, and 0.015 per cent. of silver. The following, however, is a general statement respecting the ores :—

	Lead.	Silver.	Sulphur.
	per cent.	per cent.	per cent.
Galenas (1)	79	0.011	
" (2)	74	0.012	
" (3)	65	0.012	
" (4)	80	0.008	
Poor lead ores	26	0.060	
	27	0.020	
Quartzose ores	—	0.026	
	—	0.050	
Quartzose and pyritic ores	—	0.010	16
	—	0.015	13
Pyritic ores	—	0.540	20
Sulphuretted ores	—	0.600	31
	—	0.240	30
	—	0.035	35
Lead ores with arsenic	23	0.450	Arsenic.
	39	0.100	16
	Zinc.		
Zinc-blende	38	0.044	
	40	0.020	

The lead in the ore is only paid for when it reaches 15 per cent., additional payment being made for every 5 per cent. above 20 per cent.—that is, for 25, 30, 35, and so on. Those ores in which only the silver or gold is of a value sufficient to cause them to be paid for are called "Dürrerze," and the class is subdivided into—pyritic, 20 to 40 per cent. sulphur; quartzose, 10 to 19 per cent. sulphur; and spathose, 0 to 9 per cent. sulphur.

The sulphur is paid for when it exceeds 24 per cent., and every additional 5 per cent. is paid for. Each per cent. of copper is paid for, but fractions of 1 per cent. are not taken into account.

The zinc-ores must not contain more than 5 per cent. of lead, and in ores that are not described as zinc-ores, only 3 to 4 per cent. of zinc may be present.

The copper-ores contain from 1 to 15 per cent. of copper, arsenical-ores from 10 per cent. arsenic, zinc-ores from 30 to 40 per cent. zinc, sulphur-ores from 25 per cent. sulphur.

The arsenic in an ore is paid for when it reaches 10 per cent., and fractions of 5 per cent. are accounted for.

Gold is paid for from 0.0005 per cent. and upwards, and silver 0.004 per cent. and upwards.

The weighing takes place in the presence of representatives of the mine and of the works. About 5 cwt. is weighed at a time. The accuracy of the weighing depends on the richness of the ore;

0.01 to 0.05 per cent. silver accurate to 10 lbs., 0.50 to 5 per cent. silver accurate to 0.1 lb., 5 per cent. and upwards, accurate to 0.02 lb. Ores rich in gold are always weighed to 0.02 lb.

Sampling.—A small scoopful is taken from every 2 cwt. and is thrown into two or more wooden dishes, according to the amount weighed off. The ore is then put into the ore-house, and a board is inserted in the ore-heap, showing the character of the ore, its quality, &c. The moisture is determined by heating 75 grammes in a copper shovel; the calculation of the moisture is accurate to $\frac{1}{2}$ per cent. The mixing takes place in the ore-house. The various ores are spread out in layers, the thickness of which depends on the nature of the material, layer over layer. Then a definite portion is cut off one end of the heap, and the ore so removed is thrown up into a conical heap, which is then considered to be sufficiently mixed.

Roasting.—A charge for roasting and smelting may contain 2500 cwt. roasted material from the Gerstenhöfer furnaces, 600 cwt. roasted residues from kilns and arsenic furnaces, 3000 cwt. raw ore, 200 cwt. residues from zinc-smelting.

Heaps of from 6000 cwt. to 7000 cwt. supply four roasting-furnaces for a week and a half; one furnace will treat 180 cwt. a day. The roasting-furnace is a single-bedded reverberatory, upwards of 40 ft. long and about 10 ft. broad; it has eleven doors on each side, and one, which is used for roasting pure galena, has fifteen doors on each side. It is worked from both sides at the same time. The fire-bridge is hollow, and the bed consists of a layer of fire-bricks, made from two parts of raw and one part of burnt clay; they contain 60 to 70 per cent. of silica. These bricks rest on common bricks supported by an iron plate, resting in turn on pillars. If the hearth, or fire-bridge, becomes worn the work is not stopped, but, by means of a long iron ladle, a ball consisting of one part of clay and two parts of poor quartz-ore, is inserted. This is beaten down so as to repair any defective place.

Each charge of ore consists of 34 cwt., and there are five such charges on different parts of the furnace-bed at one time. The charge near the fire-bridge is allowed to clot, and is then removed. The other charges on the furnace-bed are then advanced towards the fire-bridge the distance of two doors at a time. The fire-place is divided in the centre, so that really there are two fire-places, or grates, to each furnace, as the breadth is too great to permit one fireman to stoke the whole.

These long-bedded calcining furnaces are in connection with long brick chambers for the condensation of the fume, the collection of which takes place every six months, when some 2700 cwt. to

3000 cwt. of material is collected, containing—0.01 to 0.02 per cent. silver, 10 to 28 per cent. lead, 40 to 50 per cent. arsenious anhydride. The sulphurous anhydride from these flues cannot be used, as the gases are far too dilute and impure.

The charge for roasting generally consists of—galena 30 to 40 per cent.; poor lead ore 20 to 30 per cent.; poor quartzose ore 10 to 15 per cent.; and residues 5 to 10 per cent.

The cost of roasting each hundredweight of ore is as follows:—Fuel, 1*d.*; transport, 0.7*d.*; wages, 2.5*d.*; wear and tear, 0.1*d.*; tools, 0.5*d.*; total, 4.8*d.*

The roasted ore still contains from 5 to 7 per cent. of sulphur when the semi-fluid charge is withdrawn from the furnace into barrows of sheet-iron. The roasted charge is tipped out when solid, and broken into pieces about the size of the fist, and sorted by sight into (1) well roasted, (2) ordinary, and (3) badly roasted, according to whether much or little undecomposed galena is seen to be present. The men are paid accordingly.

There are several large Pilz furnaces, each with eight tuyeres, and one small one with four tuyeres. The following is a charge for the ore-smelting:—Ore, 450 cwt.; pyritic ore, 80 cwt.; roasted residues, 40 cwt.; slag, 550 cwt.; quartzose ore, 20 cwt.; total, 1140 cwt. This gives 88 cwt. of argentiferous lead, containing 0.4 to 1 per cent. of copper, and 20 cwt. of regulus, and very often a speise forms as well. In charging, the coke is thrown towards the centre, and the larger pieces of ore to the side.

If an obstruction or "bear" forms in the furnace, it is usually a ferruginous one; but it may contain much zinc-sulphide, and it generally forms at the top of the boshes. In order to remove it, bricks are removed below the bear, and the obstruction is knocked away while hot. The bear often has the form of a ring. The hearth of the furnace is built upon an iron plate. Then follow three layers of common bricks placed flat, and then two layers of fire-bricks, these together being about 16 in. thick. Then follows another layer, 16 in. thick, of the fire-bricks already described. The pressure of the blast is about 10½ to 13½ inches of water when smelting ore, and 7 to 10 inches when smelting slag. For driving the blast there is a twenty-horse-power water-wheel, used during the day for the liquation- and refining-furnaces, and during the night for the blast-furnaces; it also drives a small water pump. There is also a twenty-horse-power steam-engine for the blast- and liquation-furnaces, a fifteen-horse-power steam-engine for the blast-furnaces and smithy, and an eight-horse-power steam-engine for the blast-furnaces and steam-lift.

In twenty-four hours each blast-furnace smelting ore treats about 1400 cwt. to 1500 cwt. The charge would consist of—roasted ore, 600 cwt. to 700 cwt.; slag from previous smelting, 500 cwt. to 560 cwt.; and other additions, 250 cwt. to 300 cwt. This charge requires some 115 cwt. to 120 cwt. of coke, or about 1 cwt. of coke to 12 cwt. of the ore-charge. The result of the smelting is about 115 cwt. of lead, and 36 cwt. of lead regulus.

The charge described above is worked by five men at each furnace. They work in shifts of twelve hours. Below, one smelter and three assistants; above, one charger. The wages amount to about $\frac{1}{2}d.$ for each cwt. of ore.

The hearth is allowed to fill until some of the regulus is seen to come out with the slag, which is tapped continuously from one or other of two tap-holes.

The lead contains	.	.	0.5 to 0.6	per cent. of silver
The lead regulus	.	.	25.0 to 30.0	" " lead
			6.0 to 15.0	" " copper
			0.2 to 0.25	" " silver

The slags contain 0.3 per cent. of copper, 4 to 5 per cent. of lead, 0.003 to 0.004 per cent. of silver.

Smelting the Rich Slag.—The slags may be viewed as three equivalents of monosilicate with one equivalent of bisilicate, and slags that do not contain more than 0.001 to 0.002 per cent. of silver, and 1.5 per cent. of lead are thrown away.

The charges in slag-smelting are very varied. The following are examples :—

(1) Slag 900 cwt.; plumbiferous material 45 cwt.; broken-up hearths 12 cwt.; which yielded 52 cwt. of poor lead, 85 cwt. of coke being required.

(2) For every 2 cwt. of a mixture of 5 cwt. roasted regulus from slag, 12 cwt. roasted ore-regulus, 2 cwt. roasted copper-regulus, and 5 cwt. roasted liquation residues, is added $4\frac{1}{2}$ cwt. of slag from galena-smelting, and 4 cwt. of common slag.

(3) Three cwt. of ore-slag, 3 cwt. of various residues rich in lead, $1\frac{1}{2}$ cwt. once-roasted ore-regulus, 0.5 cwt. of coke. To this charge there is added, in the working-day of twenty-four hours, 12 cwt. of marl, 12 cwt. of hearth, and 12 cwt. of lead-skimmings.

(4) Twelve cwt. of slag, 25 cwt. of twice-roasted regulus, 40 cwt. of slags from the smelting of the litharge.

Products of the Slag-Smelting.—Slag-lead containing 0.4 per cent. of silver, regulus containing 10 to 20 per cent. of lead, or

regulus containing 20 to 30 per cent. of copper, poor slag containing 0.0015 per cent. of silver and 1.5 to 2 per cent. of lead.

Sometimes a speise of nickel and cobalt is also formed. The regulus is only about one-third of the amount of lead produced. The slags often contain 9 per cent. of oxide of zinc. The regulus is broken up and roasted in kilns, or stalls, and is then added to a smelting charge similar to that by which it was formed, or is concentrated in a Pilz furnace, or goes to a reverberatory for concentration with silica and barium-sulphate.

Smelting the Speise.—The charge in 150 cwt. of speise, 675 cwt. ore-slag, 4 cwt. impure litharge, 44 cwt. lead residues, 5 cwt. hearth, 40 cwt. fluor-spar, 75 cwt. coke. The products are 54 cwt. of lead, 12 cwt. concentrated speise.

The speise is concentrated by continuous and alternate roastings and smeltings, until it contains 20 per cent. of nickel, when it is sold. The poor lead goes to the liquation-furnace. The regulus is roasted in kilns and stalls, then fused to concentrate it, until it contains 30 per cent. of copper; it is then called "copper" regulus. It is afterwards treated in a reverberatory to form pimple metal. Incidentally, large quantities of impure lead and substances containing lead-oxide are produced.

The process employed for the reduction of the lead from such substances consists of a reducing-fusion. One such substance, the litharge derived from the rich argentiferous lead, contains about 78 per cent. of lead. The furnace used is a small Pilz furnace with four tuyeres. The charge in twenty-four hours is, 1500 cwt. litharge, 450 cwt. lead-slugs, 50 cwt. slags from a previous smelting, 130 cwt. coke. The products are, (1) a variety of lead, which, according to its purity, is either first liquated and then refined, or is taken to the Pattinson pots, and (2) a slag containing 10 per cent. of lead. Part of this slag goes to the next charge, and part to the first ore and slag smelting.

Liquating the Impure Lead.—This is done at Freiberg on the inclined bed of a reverberatory furnace, 500 cwt. being treated daily. The copper, with some lead, remains solid in the form of liquation-residues. The lead, before the liquation, contains 0.5 per cent. copper, afterwards it still retains 0.07 per cent. The residues are about 5 per cent. of the total lead; they consist principally of lead with 15 to 18 per cent. of copper, and are added to the slag-smelting in the Pilz furnace.

The scum from the Pattinson pots is also treated in this reverberatory, in admixture with lignite. When antimonial lead is liquated the temperature must be kept low, but a little

wood must be kept kindled in the well of the furnace to prevent the lead solidifying.

If the lead contains 1.5 per cent. of silver, it is cupelled at once—that is, it is added to lead that has been already enriched by the Pattinson process. If it is impure, the lead is refined and Pattinsonised.

In refining, the lead is fused in an oxidising atmosphere on the bed of a reverberatory furnace. The products are a variety of different kinds of litharge to which the name of "*Abstrich*" is given. They are nothing but impure litharge, and as the nature and proportion of the impurities vary greatly, the appearance is very dissimilar; some are dark-grey and stony, others are light-yellow and are crystalline in structure:—(1) Powdery tin *Abstrich*; (2) fused tin *Abstrich*; (3) arsenical *Abstrich*; (4) antimonial *Abstrich*; (5) impure litharge *Abstrich*; (6) pure litharge *Abstrich*. There is a fractional oxidation of the various impurities, the tin and arsenic going first. The time required to refine 400 cwt. of lead is about fifty hours.

The products, in the case of lead smelted from ore, are as follows:—10 cwt. of tin *Abstrich*, or about 3 per cent. of the total lead, containing 11.3 per cent. of tin, 14.4 per cent. of arsenic, 2.8 per cent. of antimony; 20 cwt. arsenical *Abstrich*, or about 5 per cent. of the total lead, containing 8.5 per cent. of antimony, 8.9 per cent. of tin, 8.7 per cent. of arsenic; 10 cwt. of antimonial *Abstrich*, about 3 per cent. of the total lead, containing 6.8 per cent. of antimony, 1.3 per cent. of tin, 4.4 per cent. of arsenic; 10 cwt. impure litharge, about 3.2 per cent. of the total lead, containing 3.1 per cent. of antimony, $\frac{1}{2}$ per cent. of tin, 2.0 per cent. of arsenic.

In refining lead produced from the smelting of slag, very similar varieties of *Abstrich* are obtained, except that they are not so rich in tin, as when lead from ore is refined. At the Halsbrücke Works, a hollow pipe through which steam is passed is sometimes used as a mechanical stirrer when refining. In desilverising the tin *Abstrich*, about 90 cwt. of slag-lead is placed on the bed of the refining furnace and then, on that, 15 cwt. of the *Abstrich*, mixed with 4 per cent. of coal; the charge is melted down in three hours, and then another 15 cwt. of *Abstrich* and 4 per cent. of coal is added, and so on until the furnace is full. The desilverised *Abstrich* is taken off (the silver passing into the lead) and run down in a small Pilz furnace.

The lead is refined and Pattinsonised. The antimonial *Abstrich* is desilverised in the same manner, except that 24 cwt. of it is

added instead of 15 cwt., as it melts easier. The arsenical *Abstrich* and impure litharge are directly revived by being run down in a small Pilz furnace for metallic lead, the lead obtained being then refined. The impure lead is added in part as a plumiferous addition to the Pilz furnace smelting ore.

The desilverised tin *Abstrich* is smelted in a Pilz furnace, the charge being 100 parts of *Abstrich* to 100 to 150 parts of poor lead-slag, 50 per cent. of slags from the same working, and 20 per cent. of limestone. The lead obtained is revived and poled in a Pattinson pot. The various kinds of *Abstrich* obtained are desilverised over and over again, until they contain comparatively no silver. The composition of the hard lead obtained from the stanniferous *Abstrich* is very varied. One variety contains 18 per cent. of tin, 10 per cent. of antimony, and 2 per cent. of arsenic.

The desilverised antimonial *Abstrich* is smelted in a Pilz furnace with slag and 10 per cent. of limestone. In twenty-four hours, 100 cwt. to 150 cwt. are sent through. The hard lead is liquated and poled, and contains about 10 per cent. of antimony, 3 per cent. of arsenic, and 1 per cent. of tin. Each refining-furnace is worked by one refiner and two assistants.

Pattinson Process as conducted at Freiberg.—In this process, the silver is concentrated in fluid lead by straining off crystals of lead which separate from the bath. The pots have a thickness at the bottom of 2.36 to 2.76 inches, and 1.9 inch at the sides. They are 5 feet in diameter at the top, and 2 feet 9 inches at the bottom. They hold about 15 tons, and last about 500 crystallisations. Each pot has a separate fire; there are sixteen pots, sometimes worked in two batteries of eight pots each. They are worked by the one-third system. Each pot is kept at a determined percentage of silver, and assays are made daily. When fresh lead is added, it is introduced into the pot containing the same percentage of silver. At Freiberg it is usually the third pot from the left. The rich lead contains from $1\frac{1}{2}$ per cent. to 2 per cent. of silver, and the poor 0.0018 per cent. The scum from pots 1 to 4 is liquated by itself, and similarly those from pots 5 to 8, and from 9 to 15 by themselves. In a case in which the enrichment had not been carried far enough, the following were assays of the contents of the pots:—(1) 1.07 silver, (2) 0.80 silver, (3) 0.42 silver, (4) 0.33 silver, (5) 0.30 silver, (6) 0.26 silver, (7) 0.18 silver, (8) 0.11 silver, (9) 0.08 silver, (10) 0.04 silver, (11) 0.02 silver, (12) 0.012 silver, (13) 0.007 silver, (14) 0.0035 silver, (15) 0.0015 silver, (16) 0.001 silver. The poor lead never contains more than 0.05 per cent. of copper, 0.2 per cent. of iron, and traces of arsenic and antimony. The fuel used is a mixture of lignite and small coke. To each battery of

sixteen pots there is one fireman, and to every two pots there are two men. There is also one lead ladler. The men work for eleven hours, but the fireman works for twelve hours.*

Cupellation at Freiberg.—The hearth is formed of 48 cwt. of fresh marl mixed with $\frac{1}{2}$ cwt. of clay. The marl is of three kinds:—

	I.	II.	III.
Calcium carbonate . . .	50	68	66
Magnesium carbonate . .	13	27	6
Iron carbonate . . .	2	2	2
Clay	14	3	25

Any pyrites present is carefully removed.

The greatest depth of the hearth from a line on a level with the tuyeres ought not to be more than 7.8 inches. The fire-resisting material with which the roof is lined consists of one part of clay and two parts of silica; 100 cwt. to 200 cwt. of lead is placed on the damp hearth, and this is covered with sawdust and chips; the roof is then put on, the wood lit, and the roof luted on with clay; the fire is kindled, and the blast turned on; the lead melts down in sixteen to eighteen hours. The temperature is gradually raised, and lead is added, 700 cwt. being the total charge. The litharge, as it forms, is removed until the remaining lead on the bed contains 60 to 80 per cent. of silver. This is taken out, and the extraction of the silver completed on a similar but much smaller hearth. If the red litharge obtained contains less than 0.02 per cent. of silver, it is sold. It is said that if the lead contains 0.2 per cent. of bismuth no red litharge will be produced. At the end of the process, where the concentrated lead and silver settle on the hearth, there is a dark spot which indicates the presence of bismuth, and which is broken away and the bismuth subsequently extracted, this portion of the hearth having been previously hollowed to collect the rich lead. There are two men attending to each furnace, and they are paid a little over a penny for every hundredweight of lead treated. It takes 120 to 140 hours to cupel 700 cwt. of lead. The silver obtained is granulated by running it into water. It is about 990 fine, and is sent to the Halsbrücke works to have the gold parted from it.

Solution of the Regulus.—The concentrated copper regulus is sent to the Halsbrücke works, where it is roasted nearly sweet. It still contains about 1 per cent. of sulphur. It is then passed through a rather fine sieve, and the larger pieces are crushed and re-roasted. The roasted regulus is dissolved in sulphuric acid in

* Pattinson's process is now supplemented by Parkes' process, a joint-process being used, but this is not indicated in the scheme.

wooden vats lined with hard lead. The sulphate of copper is crystallised out, and, after purification by re-crystallisation, is sold. Such copper-sulphate as does not crystallise out but remains in solution is removed by scrap-iron. The solution of copper-sulphate before crystallisation is made to pass over metallic copper, in order to remove any silver it may contain. The residue, after the treatment of the regulus with sulphuric acid, contains the lead, and most of the silver originally present in the regulus treated. This is sent back to the Pilz furnace, with a view to concentrate the silver in the lead produced from the lead ores.

The student would consult with advantage two papers recently published giving an account of American practice in smelting argentiferous lead.* It appears to be possible, in smelting complex ores, to collect the whole of the precious metals in lead, even if the lead present does not exceed ten or even eight per cent. of the charge. Copper is also employed with success as an agent for collecting the precious metals, and this may be effected if the copper only forms five per cent. of the charge.

Hitherto lead has been used in blast furnace smelting for the purpose of collecting the precious metals, but it appears that ores containing copper in an oxidized condition may, under certain circumstances, be smelted with other ores rich in silver, the copper of the former serving as the vehicle for concentrating or extracting the whole of the precious metals from both classes of ore, just as the lead that is employed in the ordinary process. The extraction of the gold and silver is quite as perfect as when lead is used, and there is no loss by volatilization, but the loss of metal in the slags is of greater relative importance in the case of copper than in that of lead, on account of the higher intrinsic value of the former metal. This disadvantage is, however, compensated by the fact that the rate of concentration may be increased to as much as twenty to one as against ten to one which is the maximum ratio when lead is used. The greatest drawback to a general application of the process, is the scarcity of ores that are rich in the precious metals, which are not suitable for milling, and that are at the same time free from sulphur and lead.

Not more than one per cent. of sulphur should be present,

* (1) H. F. Collins on "Smelting Processes for the Extraction of Gold and Silver from their Ores"; (2) S. W. Malcolmson, "Erection of Silver Lead Works in Mexico." "Proc. Inst. Civil Engineers," vol. cxli., part 2, 1893.

while, if the percentage rises to four or five, the operation at once becomes that of the ordinary smelting for regulus, and all advantage is lost. The presence of lead, on the other hand, gives rise to much trouble and expense in the subsequent operations of refining, hence it is not permissible to allow more than one per cent. of lead to be present in the ore charge.

Wet Processes for Treating Argentiferous Copper Ores.—In certain cases copper pyrites is converted into copper sulphate by the action of air and moisture. The sulphate

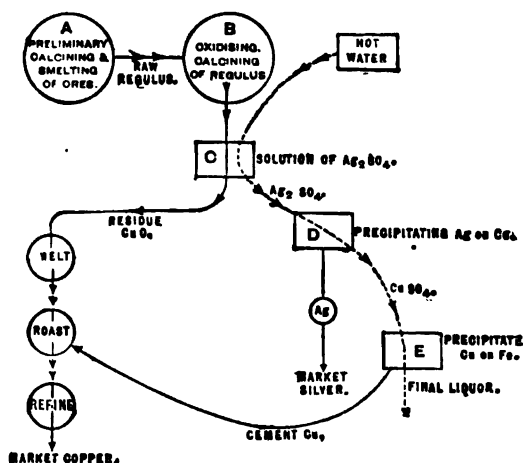


FIG. 80.

is dissolved in water, and the copper precipitated from the solution by iron. When, however, argentiferous ores are dealt with, containing much copper but not much lead, the processes are more complicated. The principal processes in vogue are :—

1. Ziervogel's process, which consists in submitting the regulus to an oxidising roasting, yielding cupric oxide and silver sulphate. The latter is dissolved in water and precipitated on copper. The cupric oxide is recovered from the residues by smelting (Fig. 80).

2. Augustin's process, which consists in submitting the regulus

to an oxidising and subsequently to a chloridising roasting, yielding cupric oxide and silver chloride. The latter is dissolved in hot brine and precipitated on copper. The cupric oxide is recovered from the residues by smelting (Fig. 81).

3. Longmaid's or Henderson's process, which is applied to the ore after roasting, and which consists in dissolving the copper and silver from the ore roasted with salt by water and dilute hydrochloric acid. The copper is precipitated by scrap iron, and the silver is recovered by the Claudet process (Fig. 82).

4. In Claudet's process the silver is precipitated as silver iodide from a solution of copper and silver chlorides by zinc iodide

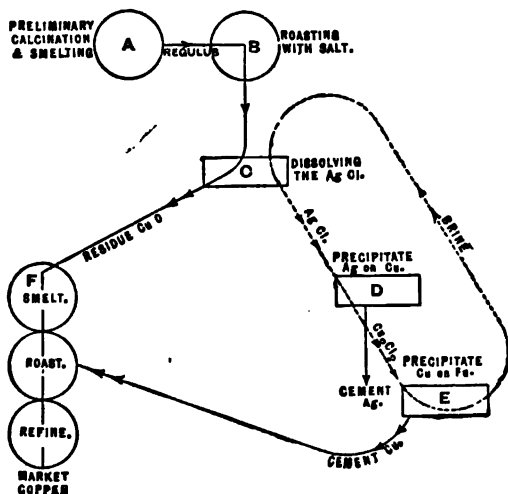


FIG. 81.

regenerated during the process, zinc being used to precipitate the silver.

These four processes are illustrated by the accompanying schemes, Claudet's process forming part of the scheme (Fig. 82).

The plant used in the Ziervogel process is illustrated in Fig. 83.

The charge of roasted material is placed in tubs A, provided with false bottoms, and hot water is introduced through the pipe *b* until the liquors begin to flow through the tap *c*. The pipe *b* is then closed, and acidulated hot water is admitted through the pipe *a*. The silver sulphate solution flows into a long tank, divided into two compartments B, C, whence it is distributed into

precipitating tubs D, provided with false bottoms on which cement copper is placed, with copper bars above it. Most of the silver is precipitated, and the liquors pass to a trough E, on the bottom of which is a layer of pieces of sheet-copper, and thence to the tubs F, also containing a little copper. The desilverised liquors are conveyed by the gutter *g* to a leaden pan, and again utilised. The precipitated silver is treated with sulphuric acid in the tubs H, and finally washed with hot water. The liquors rise through L, and are conducted by the trough M over metallic copper into tanks containing scrap-iron. The water from the

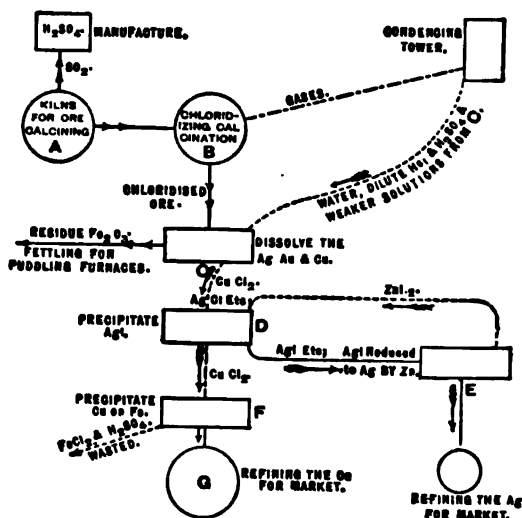


FIG. 82.

final washing is run off at N, and conducted to a lead-lined tank. The silver is moulded into blocks and refined.

Treatment of Gold Ores.—Plattner's method of extracting gold from its ores by means of chlorination is based on the fact that chlorine gas transforms gold into soluble gold chloride without sensibly attacking the earths or metallic oxides with which the gold is mixed.

The ore is crushed and roasted with salt, 5 to 9 lbs. of salt per ton of ore having been added. Any lead, bismuth, or silver present is thus converted into chloride. The iron sulphide present, however, will first be converted into iron sulphate, and this

must be decomposed to form ferric oxide by raising the temperature of the roasting furnace. The base chlorides are soluble in water, and are removed by treating them in wooden vats. The residue is then acted upon in a moist state in wooden pitch-lined vats by gaseous chlorine. The gold is thus converted into chloride, but the ferric oxide remains unchanged. The gold chloride is dissolved in hot water, and precipitated by ferrous sulphate solution in another set of wooden vats. The insoluble residues left in the "gassing" vat are now treated with sodium hyposulphite solution in order to remove the silver chloride, which may be precipitated by means of calcium sulphide, and reduced by heating in air.

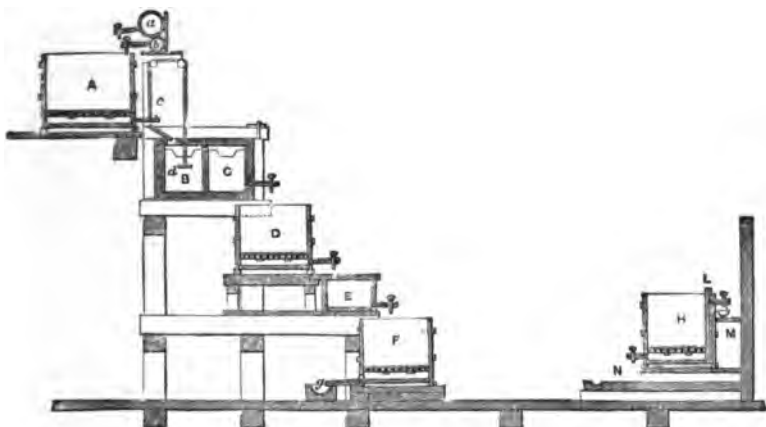


FIG. 83.

Numerous modifications of the chlorination process have been introduced, and large sums of money have been sunk in the formation of companies to work the processes. Only indifferent results have, however, been obtained.

Dr. Mears, of Philadelphia, was the first to lay stress on the influence of pressure in increasing the solvent action of chlorine. With certain ores, however, it has been found that as good results are obtained without pressure as with the highest pressure.

The largest chlorination plant in the world is at the Mount Morgan mine in Queensland. According to M'Dermott and Duffield,* the ore averages 5 oz. of gold per ton, and 1500 tons

* *Losses in Gold Amalgamation*, London, 1890, p. 30.

is worked per week, while the tailings contain only 3 dwt. per ton. The process consists in drying, crushing between rolls, roasting, and working in revolving barrels by the aid of chloride of lime and sulphuric acid. The total cost is 30s. per ton. The ore is roasted for two and a half hours, and worked in wooden barrels $5\frac{1}{2}$ feet in length. Each barrel takes a charge of 1 ton of ore, with 30 lbs. of chloride of lime, 33 lbs. of sulphuric acid, and 80 gallons of water. The gas pressure does not exceed 20 lbs. per square inch at its maximum development. The barrels are slowly revolved for two hours, and the charge is then filtered on gravel and sand beds, and the solution precipitated by filtration through charcoal filters, which are subsequently burnt in a reverberatory furnace.

A very simple process has of late years come into much prominence for the recovery of gold from the "tailings" from amalgamation plant working upon pyritic ores. It consists in the treatment of the mass of finely divided pyritic material with a very dilute solution of potassic cyanide for a period of about twenty-four hours. Cyanide of gold is formed, soluble in the excess of reagent, and the solution is run over metallic zinc upon which the gold is precipitated. By this means very large quantities of gold are now annually recovered that would, owing to the cost of treatment by the older methods, have otherwise been lost.

Purification of Platinum.—The methods of treating the metals of the platinum group present features of much interest; the use of both "dry" and "wet" operations being involved. The crude native metals are first treated in a reverberatory furnace, with an equal weight of galena. Some of the lead will be reduced to the metallic state by the iron present in the charge, and will form an alloy with the platinum, rhodium, palladium, and some of the iridium present. Any osmiridium present will not alloy, but will settle down to the bottom of the fluid mass; whilst the earthy impurities are fluxed off by the addition of glass and borax. Litharge is then added to oxidise the remaining sulphur, the slag is skimmed off, and the metal is run into ingots. The metal is then cupelled, and yields platinum and the other members of its group. To purify the mass it is melted with six times its weight of pure lead; is granulated, and treated with dilute nitric acid. The insoluble black powder forming the residue, contains all the platinum and iridium present in the lead, together with small quantities of the other metals, and is treated with dilute *aqua regia*, which dissolves out the platinum and the residue of the lead, but does not attack the iridium. The solution of chlorides is filtered off, evaporated to a small bulk,

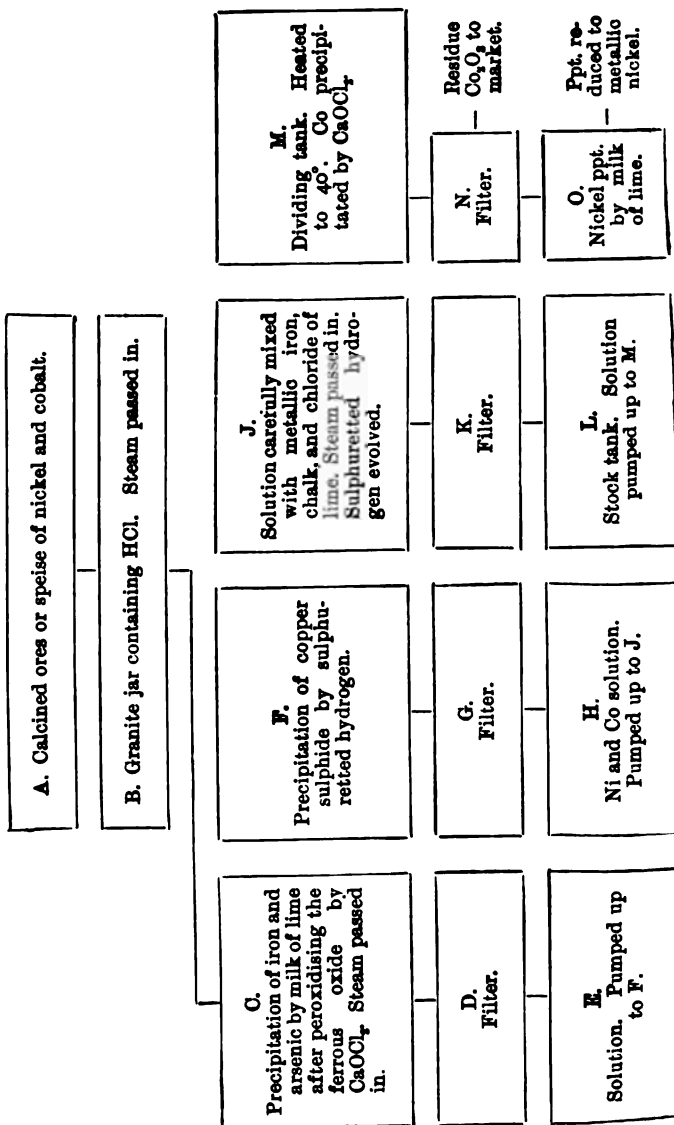
and the lead precipitated by sulphuric acid. A mixture of sodium and potassium chlorides is added to the filtrate, which is then heated to 80°C . and left to stand for several days. Most of the rhodium present remains in solution, and the precipitate of platinum-potassium chloride is collected and washed with a solution of ammonium chloride, and then with water. As some rhodium may still be present, the chloride is dried, and mixed with potassium bisulphate and a little ammonium sulphate; the whole is then heated in a platinum vessel until the platinum is completely reduced. The mass is thoroughly washed with water, and the rhodium removed as soluble bisulphate, the pure platinum sponge is finally melted under the oxyhydrogen blowpipe upon a lime crucible.

Wet Process for Treating Nickel and Cobalt Ores.—The wet methods for the extraction of nickel and cobalt from a complex regulus or arsenide consist, in the first place, of a roasting operation having for its object the volatilisation of the sulphur and arsenic, and, it may be, antimony and the conversion of the iron, nickel, cobalt, and other metals present into oxides. Ferric oxide formed in this manner at a high temperature is but little soluble in acids, whilst the other oxides may be readily dissolved. On treating the roasted material repeatedly with hydrochloric acid or with dilute sulphuric acid, a residue is obtained containing but little or no cobalt or nickel, and consisting mainly of ferric oxide. Some iron will, however, have passed into solution. Should the solution contain lead, bismuth, or copper, these metals may be precipitated by sulphuretted hydrogen; but it is customary to precipitate the copper at a later stage of the operations. The bismuth, too, may be precipitated from a hydrochloric acid solution by dilution with water.

The next operation consists in the precipitation of the iron. Any ferrous oxide which may have passed into solution is converted into ferric oxide by careful addition of chloride of lime, followed by the addition of lime, which precipitates the iron. Arsenate of iron is, at the same time, also precipitated if arsenic is present. Should the temperature of the solution exceed 40°C . some nickel and cobalt are precipitated, as also is some copper.

Instead of an addition of lime as a precipitant, caustic soda or sodium carbonate is occasionally employed to prevent the precipitation of calcium sulphate when working with sulphuric acid solutions. Care must be taken to avoid using an excess of the precipitant as the precipitation is a fractional one, and as soon as the iron has been precipitated oxides of the other metals present begin to be thrown down.

WET PROCESS FOR EXTRACTING NICKEL AND COBALT.



The next stage of the process consists in the precipitation of the copper. This is effected by raising the temperature of the solution to 70°C ., and then precipitating the copper by the careful addition of either calcium carbonate, milk of lime, or a solution of soda. If an excess of the precipitant is employed, nickel will be thrown down. When a test with potassium ferrocyanide shows that the whole of the copper has been thrown down, the cobalt is precipitated from the filtered solution by the careful addition of a solution of chloride of lime to the perfectly neutral, hot, and not too dilute filtrate. If too much chloride of lime is added the precipitate becomes nickeliferous, and this must be carefully avoided. The nickel is next precipitated, either by calcium carbonate, milk of lime, or soda. The nickel hydrate is filtered, dried, heated with sodium carbonate, to decompose any calcium sulphate that may be present, washed with acidulated water, and finally dried and reduced by carbonaceous materials to the metallic state.

This process, being dependent on the fractional precipitation with the same precipitants of the several metals present in the ore or metallurgical product under treatment, is frequently subject to slight alterations of procedure, and the following is a description of the process as carried out at a works in the United Kingdom:—

About 3 cwt. of fine ore or speise A, that has been thoroughly roasted, is charged with hydrochloric acid in granite jars, into which steam is passed. The mass is kept boiling for twelve hours. It is allowed to settle, and run off into tubs C. Steam is conducted into the tubs, and when the liquid begins to boil, bleaching powder (chloride of lime) is added to peroxidise the iron, and the mass is allowed to boil for about three hours. The arsenic and iron come down together. If no iron be present in the solution some must be added. The liquid is then run off through filters D, to underground tanks E, whence it is pumped to tanks F, in which the mass is treated with sulphuretted hydrogen. Adjoining these tanks, of which there are six, there are also three lead retorts, in which sulphuretted hydrogen is produced. In these tanks, the copper is precipitated and the nickel and cobalt solution is strained through filters G, and drains into a second underground tank H. It is then pumped into a tank J, and there successively mixed with iron, chalk, chloride of lime, and water from tubs placed above the tank, with a view to precipitate, first, any copper that may have passed into solution during filtration, and then the iron which has taken the place of the copper. The charge is first boiled by the aid of steam pipes so as to expel the sulphuretted

hydrogen. It is then run off to a tank L for stock. It is next pumped up into a dividing tank M, and heated with chloride of lime, the cobalt being precipitated as oxide at a temperature of 40° . The solution containing nickel is allowed to run off into another tank O, in which milk of lime is added, and the nickel precipitated as hydrated oxide. The liquid is allowed to run off as waste. The oxides are pumped into presses, and the water is drained off. The nickel oxide is dried on the roof of a muffle, heated, and crushed. It is then mixed with charcoal, and heated in a crucible in a reducing furnace for eight or twelve hours. A rough powder is obtained, and in this form the metal is sold, or the nickel oxide is mixed into a paste with flour and water, which is heated and cut into cubes. These cubes are placed in crucibles with charcoal, and heated to a temperature above the melting point of copper. The nickel oxide is reduced by the charcoal and by the carbonised flour. The metal does not melt, but preserves the form of cubes. The cobalt oxide is removed from the dividing tanks to stone jars, and treated by a process similar to that described, so as to remove the last trace of nickel. The cobalt is finally sent to market in the form of oxide.

System of Teaching Metallurgy.—As the choice of a particular course of metallurgical study is of much importance to the student, it will be well to consider the various systems which have been adopted for teaching the subject.

First, there is the one that long prevailed in the Royal School of Mines of this country, which, from its foundation in 1851 to within the last few years, trusted to lectures and ordinary laboratory work, supplemented, since 1880, by visits to some metallurgical district.

Second, there is the system which receives its fullest development in the Berg-Akademie at Freiberg, in Saxony, where the subject is studied theoretically in the lecture-room and laboratory, the main feature of the course being the attendance of the students, during a considerable portion of their time, in one or other of the celebrated works of the district in which the school is situated.

Third, there is the widely different plan adopted in certain American schools, notably at the School of Mines, Columbia College, New York, and at the Massachusetts Institute of Technology, Boston, where, in addition to lectures and laboratory work, the students actually conduct operations, often on a considerable scale, with small metallurgical plants.

This is the system which the author unhesitatingly prefers, provided that the importance of laboratory work and research is

not lost sight of. An industrial district is not, in his opinion, the best situation for the chief metallurgical and mining school of a nation. Such an institution derives great advantages from being placed in a metropolitan centre of education; but, apart from the question as to locality, it may be urged that an attempt to derive practical knowledge mainly from ordinary metallurgical works is attended with very distinct disadvantages. It is difficult to bring home to young mining engineers the fact that failures in mines and works quite as often result from errors in judgment as from the poverty of the ores, or defects in the processes, and upon this point Prof. R. H. Richards,* of Boston, well observes that the great advantage of teaching students by the aid of small metallurgical plant consists in their "finding out by their own experience that little losses taking place everywhere in the course of their work mount up enormously in their final account of stock, large works cannot afford to spoil a furnace-charge to show a student what happens from a little carelessness, and a well-regulated establishment may go on a long time without such a slip, and a student may be months at a works without finding out what is the key to its successes." At the School of Mines, Royal College of Science, this system of teaching with the aid of small plant is gradually being adopted, and there can be no question that the actual use of such appliances is most advantageous to the student, and that it enables him to acquire a better idea of the relations of metallurgical art to the sciences than is possible from mere theoretical work. As a type of such appliances the stamps for crushing quartz, and the concentrator, known as the Frue vanner, designed by Mr. R. E. Commans for the author's laboratory, have been placed as the frontispiece of this book.

The total height of the stamps is about 12 feet, and they are capable of treating from $1\frac{1}{2}$ to 2 tons of material in the course of a day. By the aid of this plant it is easy to determine what is the most effective speed to give to the stamps when working upon ores of various hardnesses and compositions. A wide range of problems connected with the concentration of minerals may be studied, and considerable insight may be obtained into the difficulties of collecting the precious metals by amalgamated metallic plates. The degree of success of each operation is, of course, controlled by the results of assays.

This system of teaching with the aid of small plant is gradually being adopted by the author, whose laboratory at the School of Mines is already fairly well equipped. It is not, of course,

* *Trans. Amer. Inst. Min. Eng.*, vol. vi., 1877, p. 510.

urged that such a metallurgical laboratory would in any sense be a substitute for the works in which alone the professional education of a metallurgist can be fully developed, and no such claim is made on behalf of the engineering laboratories of which the country now possesses so many. Their success abundantly justifies their existence, and all the arguments which have been urged in favour of the kind of training they afford, may be applied to mining and metallurgical laboratories.

It is to be hoped that the growth of such laboratories will be fostered in this country, and that other institutions will follow the example of the Technical School of Sheffield, which will possess a small Siemens regenerative furnace, in which the problems connected with the production of steel may be worked out, and the efficiency of the several methods of applying gaseous fuel may be compared.

CHAPTER XL

THE MICRO-STRUCTURE OF METALS AND ALLOYS.

MUCH attention has recently been devoted to the study of the structure of metals and alloys, which, in the main, owes its origin to Dr. Sorby. The limits of this work will not admit of more than a sketch being given of the methods of examination which have been adopted, and of the results that have been obtained. But the subject of microscopic metallography has assumed much importance, and, as it will in the future become a powerful ally of chemical analysis, it must certainly form a part of any volume which claims to be an introduction to the study of metallurgy.

In treating this subject, the author is mainly guided by the writings of his friend, M. Osmond, who stands prominently in the front rank of those who are studying the structure of metals and alloys. In this connection a paper recently communicated to the Mining and Metallurgical Congress at Chicago, has been specially useful.

As regards the history of the subject, it appears that microscopic metallography has not been developed from petrography. It is more closely connected with, and is a natural extension of the study of meteoric irons, and, as has often happened in the history of science, it appears to have had several independent origins. The publications of Dr. Sorby go back to 1864, and those of Prof. Martens to 1878. But in spite of this difference in date, the labours of the latter present all the characters of complete originality. While Dr. Sorby devoted himself to the development of a complete method of examining sections of opaque bodies under the highest magnifying powers, and the application of this method to different products of the metallurgy of iron, Prof. Martens first studied, though without neglecting the examinations of sections, the general laws of fractures, fissures, blow-holes, and crystallisation in metals. Prof. Wedding, of Berlin, has also made numerous investigations on the structure of iron and steel. Those of Messrs. Lynwood Garrison, and Dudley, are well known

in America. In France, M. Barba introduced in 1880 the use of the microscope in the works of Creusot, and gave the first impulse to the labours of MM. Osmond and Werth, who gratefully acknowledge the influence of Dr. Sorby.

Care in the preparations of the sections for microscopical examination is, of course, of the first importance. Dr. Sorby employs at the outset emery papers mounted on plate glass, using ultimately the finest grades which can be obtained. He continues the work with the fine-grained water-of-Ayr stone, then with the finest crocus, and ends with the best washed rouge, with which he sprinkles a wet cloth held upon a perfectly plain wooden backing.

Prof. Martens substitutes for emery the stone called Oelstein, largely employed by Swiss watch-makers, the powder of which he washes with great care, so as to separate it into different classes of fineness.

When the substance upon which the polishing with rouge is finished, is somewhat soft, such as cloth, leather, or parchment, and the substance polished is composed of constituents of different hardness, the surface of the latter becomes lightly engraved, the harder constituents appearing in relief.

This preliminary indication is always of great value, and sometimes suffices (as for instance in the case of cement-steel) to reveal the whole structure of the metal. It is therefore indispensable, when studying a specimen for the first time, to polish it under these conditions and then to examine it with the microscope. If, however, a perfectly plane surface is required for the purpose of studying the most delicate details, the polishing should be finished upon an unyielding support. Prof. Martens employs for this purpose mixtures of colophony with wax or pitch. Theoretically, the polishing cannot be too perfect; but perfection is not necessary as a general rule. If the emery papers or other hard materials have made some scratches deeper than others, which cannot be removed without excessive labour, these striations are recognised at the first glance; and, if they are few, they do not seriously hinder observations. It is possible, therefore, to obtain in less than a quarter of an hour a very satisfactory preparation, even without the use of any other instrument than the hand. Of course time may be gained, when many plates are to be polished, by using a small machine. Mr. Stead, of Middlesbrough, has constructed a convenient portable machine which it is to be hoped he will shortly describe.

In most cases, the structure of the specimen is not shown by polishing only, and must be made evident by physical or chemical processes which produce different effects upon its different

constituents. These processes vary with the nature of the metals concerned, and will be described in connection with certain cases.

Whatever be the methods of preparation, the sections are opaque, and their illumination under the microscope presents special difficulties which are not encountered in the study of translucent ones. Natural illumination will serve only for very low powers, which are usually insufficient for this work. Hence the microscope must be provided with special accessories.

For oblique illumination we have the well-known parabolic mirror of Sorby and the mirror of Lieberkühn, both of which may be mounted upon the objective. For perpendicular illumination recourse is had to Beck's vertical illuminator (Fig. 1, p. 355); this is a small transparent mirror *m* placed in the axis of the microscope, which receives the light through a slit *a*, *b*, and reflects it upon the objective. The lenses of the objective concentrate the light upon the object, and the latter is seen through the transparent small mirror. Prof. Martens employs for similar conditions a small prism (Fig. 2, p. 355), which was devised by M. Nacher, of Paris, for the use of the International Commission on the standard metre. With these two latter devices the illumination is almost as good for high powers as for low ones; it is possible to go to 1000 diameters or even higher.

M. Guillemin in an admirable paper on the metallography of the alloys of copper recently presented to the French "*Commission des Méthodes d'essai des Matériaux de Construction*" states that he prefers the reflecting prism adopted by Prof. Martens.*

The carefully polished specimen has to be attacked by a suitable reagent in order to develop its structure. According to M. Guillemin, nitric acid diluted to four times its volume is ordinarily employed, the metal being plunged in it in the cold for fifteen seconds. It is then rinsed in hot water, and if examination proves that the attack has been insufficient, it is again submitted to the action of the acid. In the case of sections of brass two immersions will suffice, but bronzes usually require four or five. The reagent adopted by Sir F. Abel, to which reference has already been made in a former chapter, gives excellent results. It consists of 10 grammes of potassium bichromate with 10 grammes of sulphuric acid in 100 grammes of water.

M. Guillemin prefers, however, to attack the specimen electrolytically by exposing it for a few minutes in a bath of very dilute sulphuric acid when connected with a simple Daniel cell. The

* Stahl und Eisen, No. 9, 1892, p. 406.

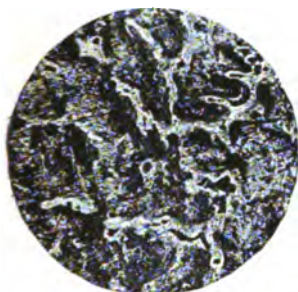
specimen is washed with hot water, then with alcohol and dried by gentle heat.

It is necessary to fix by photography the indications of the microscope. The micro-photography of minute objects has made great progress in the last few years. The first specimens of Dr. Sorby were magnified 9 diameters; those of M.M. Osmond and Werth, 18 diameters. M. Osmond, in 1890, reached 300 diameters; and Prof. Martens now goes up to 800. The equipment of the experimental laboratory at Charlottenburg, in which this remarkable result was made possible, is certainly the most beautiful and complete in existence. But much can be accomplished without costly instruments. A small microscope camera is all that is necessary, and the source of illumination may be a simple colza-oil lamp. With this crude apparatus, powers of 300 diameters may be employed; and the time of exposure (which can be reduced one-half by the use of a good petroleum lamp) does not exceed an average of 20 minutes, 40 minutes being necessary in the most unfavourable cases.

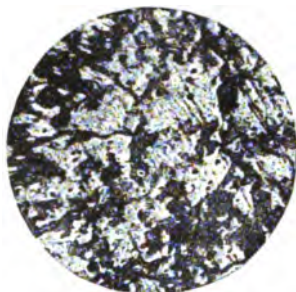
By the aid of specimens so prepared, the student may obtain precious information as to the structure of alloys. It is only necessary to bear in mind that most alloys undergo molecular rearrangement on cooling, and that distinct groups of alloys in falling out of solution often assume marked and definite crystalline forms.

In the case of the aluminium-gold alloys already described by the author, if aluminium be in large excess the purple alloy AuAl , will, on cooling, fall out in splendid crystalline arborescent forms which are readily distinguished by their brilliant colour from the grey mass through which they are distributed. M. Osmond has kindly prepared many of such sections for the author. In the case of the alloys of copper M. Guillemin has obtained results of great interest. It is known, for instance, that the qualities of the copper alloys are greatly modified by the addition of small quantities of deoxidising agents such as phosphorus, aluminium, or silicon, and the examination of etched surfaces of different samples enabled him to pronounce with certainty which deoxidiser had been employed, provided it had been used in slight excess. As an example of the appearance of the etched surfaces of copper alloys the following figures (a), (b), p. 355 are given. They both represent an ordinary bronze containing

Copper,	89
Tin,	9
Zinc,	2
Lead,	trace



(a)
BRONZE, a little Phosphorus used (as a deoxidiser).



(b)
BRONZE, a little Silicon used (as a deoxidiser).

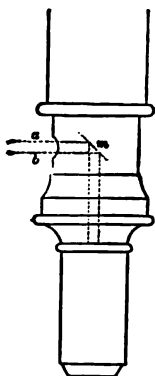
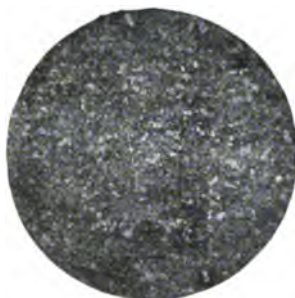


FIG. 1.
BECK'S
ILLUMINATOR.



(c)
STEEL, Hammered.

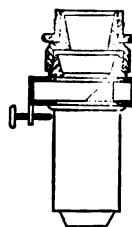
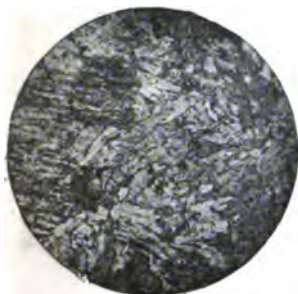


FIG. 2.
NACHET'S
ILLUMINATOR.



(d)
STEEL, Slowly Cooled.



(e)
STEEL, Hardened.

but (a) had a little phosphorus added as a deoxidiser, while in the case of (b) silicon was employed for the same purpose. The respective structures are it will be seen widely different.

The effect of thermal and mechanical treatment is also clearly shown by the microscope, and in the case of iron and steel the most remarkable results have been obtained. It has already been stated (p. 137) that Mr. Howe has proposed to give mineralogical names to the constituents of steel. Thus he calls the free iron "ferrite," the crystalline iron (or "pearly" constituent of Sorby) "pearlyte," while the carbide of iron Fe_3C is called "cementite." The microscope reveals not only the structure of these main constituents of steel, but their relative distribution in a mass of metal; and, moreover, it enables the effect of the thermal treatment of steel to be minutely studied. It would be out of place to enter into the details of this interesting subject here, and the three figures, c, d, e, shown on p. 355 are merely given as illustrations of the importance of the work. They all represent sections of the same variety of steel containing about $\frac{3}{100}$ per cent. of carbon, and all are viewed under vertical illumination, and magnified 30 diameters. (c) represents the steel after hammering, (d) after slow cooling from a temperature of 1300° , while (e) is the same steel hardened by quenching in water. It will be evident how widely different the structure is in the respective cases.

The gradual development of the cellular structure in steel under definite thermal treatment is revealed by microscopical examination. Very mild steel appears to be formed of polyhedral grains of almost pure iron, in each of which the iron presents a crystalline orientation which varies in different grains. The grains of iron appear to be surrounded by carbide of iron. As the temperature of annealing is raised, the grains at first increase in size without changing their form; they ultimately become elongated, and form a group of parallel bands.

For full details of such work which has been very briefly treated here, the student must consult the original memoirs of which the titles are given in the following elaborate bibliography, for which the author is indebted to M. Osmond.

BIBLIOGRAPHY.

- H. C. Sorby.—"*On a New Method of Illustrating the Structure of Various Kinds of Steel by Nature Printing*" (Sheffield Literary and Philosophical Society, February 1864).
 H. C. Sorby.—"*On the Microscopical Structure of Meteorites and Meteoric Iron*" (Proceedings Royal Society, vol. xiii. p. 333, and British Assoc. Report, 1865, part i. p. 139).

- H. C. Sorby.**—"On Microscopical Photographs of Various Kinds of Iron and Steel" (British Assoc. Report, 1864, part ii. p. 189).
- H. C. Sorby.**—"On the Microscopical Structure of Iron and Steel" (Dr. Lionel Beale's "How to Work with the Microscope," 4th ed., 1868, pp. 181-183).
- A. Martens.**—"Ueber die Mikroskopische Untersuchung des Eisens" (Zeits. des Ver. Deuts. Ing., vol. xxi. pp. 11, 205, and 481, Jan., May, and Nov. 1878; and vol. xxiv. p. 397, Aug. 1880).
- H. C. Sorby.**—"Lecture delivered in Sheffield's Firth College," read Oct. 20, 1882 ("The Engineer," vol. liv. p. 308, Oct. 27, 1882).
- A. Martens.**—"Ueber die Mikroskopische Untersuchung des Eisens" (Verhandl. des Ver. zur Beförderung des Gewerbfleisses, Sitzungsberichte, 1882. p. 233).
- J. C. Bayles.**—"Microscopic Analysis of the Structure of Iron and Steel" (Trans. Am. Inst. Min. Eng., vol. xi. p. 261, 1883).
- O. Dolliak.**—"Beiträge zur Mikroskopie der Metalle" (Mittheil. über Gegenstände des Artillerie und Geniewesens, 1883, Heft 9, p. 467).
- A. Martens.**—"Erläuterungen einer in der kön. Bergakademie zu Berlin befindlichen Sammlung von 120 Schiffsen zur Darstellung des Mikroskopischen Gefüges verschiedener Eisen und Stahlarten," Berlin, 1884.
- F. Osmond et J. Werth.**—"Structure Cellulaire de l'Acier Fondu" (Comptes rendus, Acad. des Sciences, vol. c. p. 450, Feb. 16, 1885).
- F. Lynwood Garrison.**—"The Microscopic Structure of Iron and Steel" (Trans. Am. Inst. Min. Eng., vol. xiv. p. 64, 1885).
- H. Wedding.**—"The Properties of Malleable Iron, deduced from its Microscopic Structure" (Journal of the Iron and Steel Inst., 1885, p. 187).
- F. Osmond et J. Werth.**—"Theorie Cellulaire des Propriétés de l'Acier" (Ann. des Mines, 8th series vol. viii. p. 5, July to Aug. 1885).
- F. Lynwood Garrison.**—"The Microscopic Structure of Cast-Wheel Iron" (Trans. Am. Inst. Min. Eng., vol. xiv. p. 913, 1886).
- H. C. Sorby.**—"On the Application of very High Powers to the Study of the Microscopical Structure of Steel" (Journal of the Iron and Steel Inst., 1886, p. 140).
- H. Wedding.**—"Die Mikrostruktur des Gebrannten Eisens" (Stahl und Eisen, vol. vi. p. 633, Oct. 1886).
- H. Wedding.**—"Die Mikrostruktur des Eisens" (Stahl und Eisen, vol. vii. p. 82, Feb. 1887).
- F. Lynwood Garrison.**—"Microscopic Structure of Steel Rails" (Trans. Am. Inst. Min. Eng., vol. xv. p. 761, Feb. 1887).
- A. Martens.**—"Ueber das Kleingefüge des schmiedbaren Eisens, besonders Stahls" (Stahl und Eisen, vol. vii. p. 235, Apr., 1887).
- H. C. Sorby.**—"The Microscopical Structure of Iron and Steel" (Journal of the Iron and Steel Inst., 1887, p. 255).
- H. Schild.**—"Die Neuesten Forschungen auf dem Gebiete der Mikroskopischen Untersuchung von Stahl und Eisen" (Stahl und Eisen, vol. viii. p. 90, Feb. 1888).
- H. Wedding.**—"Zusammenhang zwischen der Chemischen Zusammensetzung und dem Kleingefüge einerseits und der Leitungsstärke des Telegraphendrahtes andererseits" (Mittheil. aus den kön. technischen Versuchsanstalten, 1888, Ergänzungsheft i. p. 6).
- H. Wedding.**—"Ueber Fortschritte in der Lichtabbildung des Kleingefüges von Eisen und die Herstellung von Schiffsen" (Stahl und Eisen, vol. ix. Apr. 1889).
- A. Martens.**—"Ueber die Mikroskopische Untersuchung des Kleingefüges von Eisen" (Stahl und Eisen, vol. ix. p. 393, May 1889).

- F. Osmond.**—" *Le Fer et l'Acier* " (Lumière Electrique, vol. xxxv. p. 265, Feb. 8, 1890).
- H. Wedding.**—" *Das Kleingefüge des Eisens. Mikroskopische Original-photographien mit Erläuterungen* " (Berlin, 1891).
- Sir Fr. Abel.**—" *Presidential Address* " (Journal of the Iron and Steel Inst., 1891, part i. p. 18).
- F. Osmond.**—" *Note on the Microstructure of Steel* " (Journal of the Iron and Steel Inst., 1891, part i. p. 100).
- H. Behrens.**—" *Sur la Structure Microscopique et sur la Trempe de l'Acier et de la Fonte* " (Recueil des travaux chim. des Pays Bas, vol. x. p. 261, 1891).
- H. Wedding.**—" *Das Gefüge der Schienenköpfe* " (Stahl und Eisen, vol. xi. p. 879, Nov. 1891).
- A. Martens.**—" *Die Mikrophotographische Ausrüstung der kön. Mechanisch-Technischen Versuchsanstalten* " (Mittheil. aus den kön. Technischen Versuchsanstalten, 1891, Heft 6, p. 278).
- P. H. Dudley.**—" *Microscopic Structure of Steel* " (Journal of the New York Microscopical Society, Oct. 1891).
- A. Martens.**—" *Ueber Einige in der Mechanisch-Technischen Versuchsanstalt ausgeführte Mikroskopische Eisenuntersuchungen* " (Mittheil. aus den kön. Technischen Versuchsanstalten, vol. x. p. 57, 1892, Heft 2).
- A. Martens.**—" *Die Mikroskopische Untersuchung der Metalle* " (Glaser's Annalen, vol. xxx. p. 201, 1892).
- H. Behrens.**—" *Revue Générale des Sciences Pures et Appliquées* " (vol. iii. p. 343, May 15, 1892).
- A. Martens.**—" *Das Gefüge der Schienenköpfe* " (Stahl und Eisen, vol. xii. p. 406, May 1, 1892).
- H. Wedding.**—" *Das Gefüge der Schienenköpfe* " (Stahl und Eisen, vol. xii. p. 478, May 15, 1892).
- A. Martens.**—" *Das Gefüge der Schienenköpfe* " (Stahl und Eisen, vol. xii. p. 530, June 1, 1892).
- G. Guillemin.**—" *Analyse Micrographique des Alliages* " (Comptes rendus de l'Académie des Sciences, vol. cxv. p. 232, July 25, 1892).
- Tetsukichi Mukai.**—" *Studien über Chemisch-Analytische und Mikroskopische Untersuchung des Manganstahls* " (Freiberg, 1892).
- H. M. Howe.**—" *Note on Manganese-Steel* " (Trans. Am. Inst. of Min. Eng., vol. xxi., 1892).

CHAPTER XI.

ECONOMIC CONSIDERATIONS.

Object of the Metallurgist.—Viewed in its commercial aspect, the object of the metallurgist is to render science subservient to manufacturing art, or, what is equivalent, to make science remunerative. If, as has been well observed, we hope to urge on practical metallurgists the importance of combining scientific with practical knowledge, it must be demonstrated that the combination will be of pecuniary advantage to themselves, as they can have no inducement for investing capital to carry into practice an invention, however beautiful and attractive in a scientific point of view, apart from the consideration of gain. This being the case, it will be well for the student to bear in mind a few of the principles by which the relations of capital and labour are guided, and the economic conditions under which metallurgical works are carried on.

Capital and Labour.—In the early stages of the metallurgical art, when the metals were extracted from their ores either by the direct action of heat, or by the aid of simple reactions, man was, as Gruner shows, in a measure the sole mechanical agent in this industrial art; but when machines and appliances were devised, the agency of man became less apparent. In order to obtain these machines, Capital is necessary, and capital has been defined as "accumulated work," stored, that is, from some period anterior to that in which it has been brought into play. This accumulated work also demands payment when it is utilised, and this payment is the interest received by the capitalist who furnishes the equivalent of work. Manual labour is still necessary, and its influence is always considerable, even though it bears a less direct relation than formerly to the cost price of the product. It must be remembered, however, that there has always existed between capital and labour, between the employer and the employed, antagonism which it is very difficult to entirely banish. The utmost care should nevertheless be devoted to reducing it to the smallest possible limits, and as the condition of operatives

has materially improved during the last quarter of a century, it is certain that the efforts that have been made on their behalf have not proved fruitless.

There is a widespread feeling that the interests of capital and labour must be antagonistic, and as it is impossible to ignore the fact that the conflict between them is giving rise to grave apprehension, it becomes the duty of all who possess influence to strive not merely for peace, but to range themselves on the side of justice and humanity. The great labour question cannot be solved except by assuming as a principle that private ownership must be held inviolable, but it must be admitted that there was a time when capital had become arbitrary and some kind of united action on the part of workmen was needed in self-defence. If, however, we turn to the action of the leaders of trades unions in the recent lamentable strikes, we are presented with a picture which many of us can only view as that of tyranny of the most close and oppressive kind, in which individual freedom cannot even be recognised. There are hundreds of owners of works who long to devote themselves to the true welfare of those they employ, but who can do little against the influence of the professional agitator, and are merely saddened by contact with prejudice and ignorance. The view is probably correct that some system by which the workman participates in the profits of enterprise will afford the most hope of putting an end to labour disputes, and we are told that profit-sharing tends to destroy the workman's sense of social exclusion from the capitalistic board, and contents him by elevating him from the precarious position of a hired labourer. No pains should therefore be spared in perfecting a system of profit-sharing.

Pensions are great aids to patience and fidelity. Watchful care over the health, interests, and instruction of the employed is exercised by many owners of works. Workmen must not forget that the choice of their own leaders is in their own hands, and on this the future mainly depends. "We may lay it down as a perpetual law that workmen's associations should be so organised and governed as to furnish the best and most suitable means for attaining what is aimed at, that is to say, for helping each individual member to better his condition to the utmost in body, mind, and property." The words will be found in an Encyclical letter which Pope Leo XIII. issued on the "Condition of Labour," and it is specially interesting that the Bishop of Rome in his forcible appeal again and again cites the opinion of St. Thomas Aquinas, who was a learned chemist as well as a theologian

Those of us who realise that "the higher mysteries of being, if penetrable at all by human intellect, require other weapons than those of calculation and experiment," should be fully sensible of our individual responsibility. Seeing that the study of the relations between capital and labour involve the consideration of the complex problems of existence, the solution of which is at present hidden from us, we shall feel with Andrew Lang that "where, as matter of science, we know nothing, we can only utter the message of our temperament." It is to be hoped that the patriotism of the workmen will prevent them from driving our national industries from these shores, and those to whom the direction of the metallurgical works of this country is confided, may be asked to remember that we have to deal both with metals and with men, and have reason to be grateful to all who shall extend the boundaries, not only of our knowledge, but also of our sympathy.

This hope that workmen would not drive national industries from our shores was expressed in the Author's address as President of the Chemical Section of the British Association in 1891, but it is to be feared that a warning is still greatly needed. Metallurgical enterprise in this country is receiving a severe check through the misguided action of trade leaders. Belgian plates are being imported into Middlesborough, and compete with the home production. Quite recently, so trustworthy an authority as Sir Joseph Pease has addressed such a warning to *The Times*.* He says "With peace between capital and labour we shall hold our own; with war, our trade will leave us. . . . A leading firm tell me," he adds, "that they are at this moment carrying out two lines of railways in British colonies and with British capital, but all the bridge work, steel sleepers, and rails come from Germany. At Aachen, some hours distant from the coast, thousands of tons of steel sleepers are being made for English companies; 30,000 tons of rolled joists were made at Halle, in Belgium, and used in London alone last year. The roof for the Athenæum in Liverpool, and that for the new United Service Institution at Whitehall are being manufactured abroad. And this is the case whilst there are multitudes at home who cannot get work at any price, and others are refusing it even on terms to be settled by arbitration."

It will be evident that some knowledge of political economy is absolutely necessary as an "Introduction to the Study of Metallurgy," and the Author has written this in the earnest hope that the lesson that capital and labour must work together may not be learned too late.

* *The Times*, October 6, 1893.

Modes of Payment.—In metallurgical works piecework is the system generally adopted. This simply consists in paying the workman, in proportion to the amount of work executed, at a settled rate. It is the only system that conduces both to the interest of the employer and the employed. The first and most considerable difficulty consists in fixing the price of the piece, or the unit of work, and the adjustment of the contract affords abundant opportunity for the exercise of forbearance and equity on the part of the employer. The arrangement is more complicated where, instead of agreeing with a single workman, it is necessary to entrust work to several workmen associated as partners. It is then impossible to divide the work equally, for some of the workmen are more experienced than others. In this system it is also difficult to ensure that the work executed is of good quality, and careful supervision is necessary.

Remarkable results have been attained with this system at the Creusot, Terre Noire, and other French steelworks, where the wages have increased 50 to 60 per cent., and the production has been doubled in the space of a few years, and that without increasing the number of hours of work. A special stimulus, too, is given by progressive payments—that is to say, by increased payment for the supplementary tons in excess of the normal out-turn of iron or steel.

The adoption of this system of giving premiums has been attended with marked success. At the great Belgian zinc-works of *La Vieille Montagne*, all systems of payment are adopted; but the smelters and mill-men receive, in addition to a fixed wage, a premium calculated on the out-turn, and a special premium is also given for unwonted energy. In some cases, the firemen receive a similar premium, based on the time their furnace lasts without repair. In other cases the workmen receive a premium when they obtain from the ores a greater amount of metal than that which they are calculated to yield. Two-thirds of this premium is paid periodically with the regular wage. The remaining third is retained until the end of the year, and it is not paid then unless the workmen have worked regularly throughout the year.

At the Dowlais ironworks, the system of giving premiums is adopted in some instances—for example, puddlers are paid so much a ton for their work with a supplemental wage if they work a full number of turns during the week. The majority of men in iron and steelworks are paid per unit of work—that is to say, by the ton or quantity of work they turn out.

At the Royal Mint, London, a somewhat peculiar system is adopted. Prior to 1870, the workmen were paid on an average

2s. 8d. per 1000 accurately struck coins, and when the Mint was not at work they received a small payment amounting to from 6s. to 10s. per week. The objections to this system are obvious. When the department was in full work, the men received an average of £2 15s. per week, and during the remainder of the year they received allowances insufficient to maintain them, or to prevent their forming other engagements. The result was, on the one hand, that the more improvident among them contracted liabilities and returned to work in debt, and, on the other hand, that the more skilful workmen were induced to accept employment elsewhere, and the Mint lost their services. The rate paid for piecework was therefore slightly reduced, and a uniform payment of £1 per week for the men, and 10s. to 15s. per week for the boys, as "subsistence money" as it is termed, was set on foot.

There can be no doubt that the system of premiums renders it possible to retain the services of good workmen, as well as to stimulate and encourage their intelligence. It is the best method of enabling him to share in the profits, and at the same time it indirectly augments those of the employer.

We now come to a question that has been discussed with much interest in recent years. Certain economists and philanthropists urge that it would entirely remove antagonism between capital and labour, if the operatives directly participated in the profits of an undertaking. Others contend that this sharing of profits, far from effecting a better understanding between capital and labour, would only give rise to further troubles. In one shape or another participation of profits has found a good deal of favour on the Continent, where many works have adopted it with generally very beneficial results to all parties concerned. This has notably been the case at the ironworks of Godin, at Guise, France.*

M. P. Leroy-Beaulieu, editor of *L'Economiste française*, states that the system of participation in profits, viewed as a general method of organising labour, is both deceptive and dangerous. It may be possible to admit superior workmen and foremen to participation in profits; but in this country, at least, workmen are not ready for the change. Everything goes well as long as the works are carried on at a profit; but in bad times discontent soon breaks out. The system is not viewed with favour by the workmen themselves. They are perfectly willing to share in the profits, but they object to be answerable for their share of loss, and are even reluctant to contribute to a reserve fund

* *Journ. Iron and Steel Inst.* 1888, No. I. p. 102.

to cover the losses of future bad years. A workman cannot either wait for better times, or turn out products at a loss in order to retain his employment. Moreover, the final participation appears too remote; the workman cannot appreciate the relation that exists between his work and the annual profit.

Among the methods that have been adopted for giving the men a permanent interest in the works, the following may be enumerated:—

1. The method of paying over to the workmen a share in an annual cash bonus.

2. Retention of the share for an assigned period, in order ultimately to apply it, together with its accumulated interest, for the workman's benefit.

3. An annual distribution of a portion of the workmen's share and an investment of the remainder. This third method is adopted at the La Vieille Montagne zinc works, where the results have been found to be most beneficial, and have entirely prevented strikes.

Whatever method be adopted, no effort should be spared to induce the men to exercise the utmost care in the conduct of their ordinary occupations. To illustrate this, Mr. Kenward, the manager of Messrs. Chance's works, near Birmingham, states that in such an apparently routine occupation as superintending a machine punching holes in a metal plate, a thoroughly active workman could realise a surplus wage three times as great as that obtained, under identical conditions, by a less strenuous but not less skilful fellow workman. With due care, a large amount of the waste that occurs in every trade could be avoided. In metallurgical industries, this waste is often apparent, and in some cases the dimensions of the scrap-heaps are a source of wonderment to foreigners who visit this country.

Those who are not engaged in active constructive work can form no adequate conception of the enormous waste caused by inaccurate or bad workmanship, and this is well shown by the fact to which attention has recently been directed by Mr. R. Caird, of the well-known firm of engineers and shipbuilders at Greenock. He estimates that iron and steel to the value of £5,000,000 are annually wasted as "scantlings," or are employed in excess of actual requirements in shipbuilding, and he states that over £200,000 are spent per annum in propelling excessive and unnecessary material.

Quite apart from the methods of remunerating labour, much will depend upon the personal relations between employer and employed, and more especially upon the moral example set by the heads of the firm, and upon the amount of care and interest

they display in providing for the wants of their people in the way of schools, gardens, savings banks, libraries, and hospitals. In this country the provision made in this respect at such works as Crewe, Elswick, and Dowlais deserves especial commendation. At Crewe there is a well-organised institute, in which competent teachers prepare the younger operatives for the various technological examinations throughout the country. Similar institutes have been founded at many other works.

No doubt where, as in the Royal Mint and other Government establishments, pensions can be given, they afford the most powerful inducements to industry and fidelity.

It is not necessary here to dwell upon the importance of technical education. The advantages that craftsmanship constantly reaps from scientific knowledge are standing proofs of the necessity for special training. All may be summed up in a few words borrowed from the writings of a former French Minister of Finance, Jules Simon :—

“The practised eye and the sure hand are much, but they do not replace Science. The smith who knows the drawbacks of too rapid oxidation, who knows why throwing water on the surface of fuel increases the heat at the centre of the mass, the puddler who takes into account the effect of an oxidising or reducing flame, and who exposes metals to one or the other at the right moment—such are evidently the best workmen, more skilful for current needs, less disconcerted by an accident, less embarrassed by having to describe an observation, less slaves to routine, and quicker to adopt new processes.” He points to the fact that so many of the modern inventions are due to workmen, and justly urges that the more intelligent the workman becomes, the better he will understand the skill possessed by those who direct him, and the more he will appreciate work that differs from his own.

In spite of all the advantages that technical education offers, it must be remembered that many metallurgical works in this country are successfully conducted by so-called practical men; not the kind of man so forcibly described by Sir Frederick Bramwell,* as one “whose wisdom consists in standing by, seeing, but not investigating, the new discoveries which are taking place around him, the aim and object of such a man being to ensure that he should never make a mistake by embarking his capital or his time in that which has not been proved by men of large hearts and large intelligence;” nor the man who accepts no rule but the rule of thumb, but practical men possessing technical knowledge of a high order, whose careful observations enable

* *Brit. Assoc. Rep.* 1872, p. 238.

them to use the results of past experience in dealing with circumstances and conditions analogous to those they have met with before, and with which long practice has made them familiar. It would be difficult to overrate the value and importance of such knowledge as theirs, and, when we remember the scale on which smelting operations are carried on, it will be obvious that this kind of knowledge can only be gained in the works, and not in the laboratory or lecture-room, for, however careful metallurgical teaching in a school may be, it is only practical in a limited sense. At the same time, it must be borne in mind that a man trained to scientific methods starts with the enormous advantage of being able to deal with circumstances and conditions that are new to him, and with which, therefore, he cannot be said to be familiar. The technical skill that time and opportunity can alone give him will then rest on a solid basis. It is necessary, however, to guard against undervaluing the teaching of experience unaided by reasoning that we should recognise as scientific, for it is only necessary to witness such operations as the roasting of a large mass of ore on the bed of a furnace, or the forging of many tons of iron under a steam hammer, to appreciate the value of the subtle skill of sight and touch on which success depends.

The relation between scientific and technical men is thus traced, as hitherto there have been misunderstandings on both sides, or, as Dr. Williamson* well observed, "Men of detail do not sufficiently appreciate the value of usefulness of ideas or of general principles; and men of science, who learn to understand and control things more and more by the aid of the laws of Nature, are apt to expect that all improvements will result from the development and extension of their scientific methods of research, and not to do justice to the empirical considerations of practical expediency which are so essential to the realisation of industrial success in the imperfect state of our scientific knowledge."

While it is no longer necessary to justify the scientific teaching of metallurgy, it is as important as ever that the true relation of Theory and Practice should be clearly understood. It rarely happens that a process can be transferred from the laboratory to the works without important modifications; and it must be remembered that metallurgy is a manufacturing art, and that, when the truth of a theory has been demonstrated, a dividend has to be earned. This would, indeed, often be difficult without the aid of the practical man. Practical men have, however, ceased to undervalue science, and the most practical body of men in the world, in the best sense of the term, the ironmasters of

* Inaugural Lecture, University College, London, 1870.

this country, on whom its prosperity so largely depends, formed themselves, in 1870, into an Iron and Steel Institute, of which many of the members possess high scientific attainments, and are distinguished for scientific research.

Turn, then, to the advice given by those who are accustomed to deal with metals on a large scale. In 1873 Sir Lowthian Bell* stated: "If we would avoid the failure of what may be designated unscientific practice, or the failure of impracticable science, we must seek to combine commercial intelligence with a knowledge of those natural laws which form the only trustworthy groundwork of the complicated processes in which we are engaged."

Again, Sir W. Siemens,† in 1877, said, "It is not many years since practical knowledge was regarded as the one thing requisite in an iron smelter, whilst theoretical knowledge of the chemical and mechanical principles involved in the operations was viewed with considerable suspicion."

As regards the preliminary training in metallurgy, the utmost efforts of the student should be devoted to securing a thorough acquaintance with scientific methods and metallurgical principles, and, at the same time, to gathering as many well-ascertained facts as possible, remembering that applied science is nothing but the application of pure science to particular classes of problems. It consists of deductions from the general principles, established by reasoning and observation, which constitute pure science. No one can safely make these deductions until he has a firm grasp of the principles, and he can obtain that grasp only by personal experience of the processes of observation and of reasoning on which they are founded.

Production of Metals.—According to a diagram prepared by order of the French Minister of Public Works, and shown at the Paris Exhibition of 1889, the world's production of metals in 1887 was as follows:—

	Quantity. Tons.	Value. Francs.
Pig-iron	22,721,000 ...	1,155,297,000
Silver	3,383 ...	700,500,000
Gold	158 ...	629,600,000
Copper	291,000 ...	324,908,000
Lead	474,000 ...	180,785,000
Zinc	333,000 ...	129,795,000
Tin	35,000 ...	95,123,000
Mercury	3,794 ...	19,780,000

* *Journ. Iron and Steel Inst.* 1873, p. 12.

† *Ibid.* 1877, p. 7.

The world's production of coal during the same year amounted to 435,024,000 tons, valued at 3,000,652,000 francs.

The amount of pig-iron produced per head of population in the principal iron-producing countries is as follows:—

	lbs.
Great Britain	463
Belgium	282
United States	238
Sweden	207
Germany	187
France	87
Austria-Hungary	42

Price of Metals.—In an able paper,* published in 1887, Dr. D. A. Wells contends that depression in trade is largely the result of depression in the prices of metals and other metallurgical products. It is interesting, therefore, to consider past experience in the production and price of metals.

In the case of iron Sir Lowthian Bell fixed the world's production of pig-iron in 1870 at 11,565,000 tons, which increased to 14,345,000 tons in 1872. From that date production remained stationary until 1879, when it was 14,048,000 tons. After 1879 the average make for the ensuing five years was 18,000,000 tons, and in 1883 it rose to 21,063,000 tons, or nearly 50 per cent. more than it was in 1879. While the production of iron increased in the United Kingdom at the rate of 131 per cent. from 1870 to 1884, the increase in the production of the rest of the world during the same period had been 237 per cent.

Under such circumstances the price of pig-iron throughout the world has rapidly declined.

In America, pig-iron was 45 dollars per ton in 1870; in 1885 it was 16 dollars. Cleveland pig-iron was £4 17s. per ton in 1872, £2 10s. in 1880, 37s. 2d. in 1887, and 36s. in December 1893. In 1874 Bessemer steel rails were £12 per ton; in 1887 they were £4. Since 1870 there has been a marked increased production on the same expenditure in capital and labour. In Great Britain, the yield of iron per workman per year was 173 tons in 1870, 194 tons in 1880, and 261 tons in 1884. During the period under consideration, there has been a large substitution of steel for iron. A ship of 1700 tons requires 17 per cent. less material if made of steel than if of wrought iron; at the same time its efficiency is 7 per cent. greater in the former case. Again, on account of the greater durability of steel, a rail of this material has a life probably three times as long as that of an iron one. An iron rail is replaced after eight to twelve years, whilst a steel one lasts for twenty-four

* *Contemporary Review*, 1887, p. 523.

years. The consequence is that the British railways require only 200,000 tons annually of steel rails for replacement. If, however, they were of iron, 500,000 tons would be required. The same period has witnessed a great diminution in the production of puddled iron. This, it has been computed, has resulted, in the ten years from 1875 to 1885, in the loss of £4,667,000 of capital invested in puddling furnaces in England alone.

Other metals have also undergone great fluctuations in price; in most cases there has been a decline. In the case of copper, the increased annual production for the year 1885, compared with 1873, was 97 per cent., the increase being chiefly in the United States, Spain, and Portugal. In 1886 copper reached its lowest price, it having been, at New York, $9\frac{1}{2}$ cents per lb., whilst in 1880 it was 25 cents per lb. In January 1887, Chili bars cost £40 per ton. Many mines had to stop working, for at such prices they could only work at a loss. The great mines alone kept on, but their dividends were considerably reduced. This state of things led to speculation in copper, and endeavours were made to buy up a certain quantity of this metal, to raise the price, and then to sell at a profit. A syndicate was formed in Paris, and large quantities of copper were bought. The first results exceeded all expectations. Copper rose in a short time from £40 to £80. It was then resolved to make the affair permanent, and the syndicate contracted with the leading copper mines to buy their output at a given price. It undertook, in fact, to take 150,000 tons a year, involving an outlay of at least £9,000,000. Besides this, in order to keep up the price and the monopoly, it was necessary for the syndicate to buy all the output of those mines which declined to contract. One of the chief factors in the affair, however, was overlooked. Consumers did not come forward as in previous years. Copper came into the market from all directions, and, owing to the high prices, old sheathing was melted down, meeting the consumption, and copper in many cases was superseded by iron or steel. In short, the stock of the syndicate swelled daily in alarming proportions, and in February 1889 the crash came, and copper fell to £39. Since this date it steadily rose, until August 1890, when it was £60 per ton. It is now (December 1893) £54.

From 1880 to 1885, the world's production of lead increased about 30 per cent., and the price fell in the same proportion. In the latter year, there was great commercial distress among British lead miners and smelters. The price is now (December 1893) about £11 per ton.

Nickel, not many years ago, was a scarce metal of limited uses, but now the annual production amounts to from 800 to 900 tons. This exceeded the demand, and hence it was quoted at a compara-

tively low figure. The new Caledonian and Canadian ores are capable of yielding an immense supply of this metal; but until recently there has been no market for it. In January 1887 the price was 2s. 3d. per lb. In 1893 it was 2s. 6d.

From 1860 to 1864, the demand for tin exceeded the production, and consequently prices ruled high. In 1872 the price was as much as £159 per ton. The large yield of the Australian mines from 1872 to 1878 brought the price down to £52 in the latter year. Since then, however, the Australian output has diminished, but the supply from the Straits has augmented. The demand has also increased, and prices have been £110 in January 1887, £167 in January 1888. It is now (December 1893) £76.

Better plant and the revolution in the price of iron has caused the production of tin plates to be doubled for the same price during the last fifteen years. In 1872 the price per box was 26s. in 1887 it was 13s., in 1890 15s. 6d., and in 1893 12s. to 15s.

The price of mercury in 1874 was £26 per flask. In 1884 it fell to £5 2s., and in 1888 it rose to £10 7s. The decline in price of this metal was due to the increased production of California, which yielded 30,000 flasks in 1870, and 80,000 flasks in 1877. The demand for mercury in the treatment of silver ores is diminishing on account of the more general adoption of the lead method for extracting silver. It is now about £8.

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CONCLUSION.

The foregoing pages will have shown the student that the adaptation of metals for use is an important part of the metallurgic art, which is by no means limited to the extraction of metals from their ores. The author considers that in the immediate future the most marked technical advance may be expected not from improvements in smelting operations, but from the study of the properties of metals and alloys as influenced by thermal or mechanical treatment, and by the presence of foreign matter. It may be urged that such questions should be left to the Physicist and to the Engineer, but the Metallurgist must devote attention to them as their practical solution has to be effected by him, and he alone can appreciate the economic difficulties which present themselves.

INDEX.

- ABBOTT**, 26
Abel, Sir F., 56, 117, 131, 353, 358
Absorption of gases, 45
 liquids, 45
Abstrich, 336
Achard, 61
Acoustic properties of metals, 44, 47
Addy, 168
Agents, metallurgical, 205
Agricola, G., 3
Aitken coke oven, 195
Akerman, 132
Allotropic forms of metals, 90
Allotropy, 87, 120, 125, 137, 177-178
Alloys, 60, 169
 colour of, 100
 composition of (table), 105
 electrical conductivity of, 83
 electro-motive force of, 86
 freezing points of, 86
 purple, 178
Almaden furnace, 269
Aludel, 269
Aluminium, influence of, on iron, 35
 on copper, 41
 on gold, 170, 178
 bronze, 41
Amalgamation, 221
Anderson, Dr. W., 128, 167
Andrews, 20, 289
Annealing, 108
Anthracite, 183
Appolt coke oven, 192
Argentiferous copper ores, 340
Armstrong, H. E., 13
Arrhenius, 177
Arsenic, influence of, on iron, 37
Ashburner, 186
Atomic volume, 95
Augustin process, 315, 340
Aubertot, 201
BACON, Francis, 112, 120
 Roger, 3
Baker, Sir B., 50
Ball, E. J., 34, 45, 69
Balling, Prof., 210
Baly, 143
Barba, 167, 352
Barrett, Prof., 121
Barus, 121, 127, 132, 144, 150, 156
Basic Bessemer process, 272
 slag, 274
Bauxite, 227
Bayles, 357
Becker, 4, 112
Beck's mirror, 353
Bequerel, 150
Beehive coke oven, 190
Behrens, 358
Belgian zinc furnace, 268
Bell, Sir Lowthian, 159, 202, 242, 287, 367
Bessemer process, 271
 Sir H., 270
Bergman, 89, 113
Berthelot, 61, 110, 289, 293
Berthier, 117
Berthollet, 89, 114
Berzelius, 73
Bibliography of alloys, 104
 of thermo-chemistry, 312
 of fuel, 203
 of micro-structure of metals, 356
Biringuccio, 3, 61
Bismuth alloys, 88, 107
Black, 2, 115
Blast furnace, 240
Blowing engines, 281
Boghead mineral, 184
Bolley, 90
Bornstein, 57
Bosches, 241
Boston and Colorado Smelting Co., 320

- Bottons, 17
 Boyle, R., 4
 Bramwell, Sir F., 365
 Brass, strength of, 21
 Braune, 13
 Brinell, 130
 Brittleness, 17
 Bronzes, 104
 malleable, 108
 Brouncker, Lord, 4
 Brown, Cram, 5
 coal as fuel, 180
 Browne, Sir T., 130
 Brückner cylinder, 266
 Brustlein, 37
 Burton, 145
 Busek, 136

 CÆSALPINUS, 4
 Cailletet, 55, 280
 Caird, 364
 Calcination, 222
 Calculation of furnace charges, 210
 Callendar, H. L., 148, 158
 Calorie, 140, 289
 large, 290
 Calorific intensity, 141
 power, 140
 Calorimeter, 140, 171, 290
 Cannel coal, 184
 Capital, 359
 Carbon, influence of, on iron, 28, 115, 131
 Carbonised fuel, 186
 Carnegie, A., 186
 Carnelly, 145, 153
 Carves oven, 193
 Catalan furnace, 237
 Cavendish, 89
 Cementation, 269
 Chantry, Sir F., 110
 Charcoal, 186
 Chemical agents, 225
 changes in the blast furnace, 242
 energy, 289
 equilibrium, 8, 294, 296
 false, 297
 Chernoff, 121
 Chevreul, 4
 Chimneys, 278
 Chlorination, 342
 Christofle, 68
 Chromium, influence of, on iron, 37
 Circular piles, 189
 Clapp-Griffiths' converter, 274
 Claudet process, 341
 Clausius, 54
 Clémendot, 112
 Closed-vessel furnaces, 267

 Clouet, 115
 Coal, 181
 Cobalt, extraction of, 344
 Coffin, 128
 Coinage, 52
 alloys for, 104, 107
 Coke, 188
 ovens, 190
 Cold-short, 16
 Collins, H. F., 339
 Colour of alloys, 100
 metals, 42, 100
 Commans, 349
 Compressed fuels, 186
 Compression, changes due to, 45
 union of metals by, 65
 Conduction of electricity by alloys, 82
 Constants, physical, of metals, 58, 59
 Constitution of alloys, 61
 Converter, Bessemer, 269
 Coppée coke oven, 191
 Copper alloys, 105
 influence of, on iron, 34, 98
 on gold, 94
 Copper, strength of, 22
 nickel alloy, 106
 production of, 369
 Welsh smelting, 316
 wet process, 340
 Coppet, 46
 Cornu, 160
 Cort, 257
 Cowper hot-blast stove, 284
 Cramer, 113
 Crew, 185
 Critical curves, alloys, 77
 points of iron, 98, 122
 Crookes, 177
 Crova, 86
 Crucibles, 229
 Crystallisation, 43, 88
 Cup and cone, 247
 Cupellation, 2, 338
 furnace, 258
 Cyanide process, 344

 D'ARCEY, 70
 Dalton, 89
 Davy, Sir H., 136
 Debray, 92
 Definitions of iron and steel, 41
 Delta metal, 45
 Demarçay, 56
 Density, 14
 Deshayes, 28
 Deville, H. Ste. Claire, 5, 6, 54, 137, 289
 Deville's pyrometer, 154
 Dewar, J., 83

- Diamond, carburisation of iron by, 115
 Die Steels, 135
 Diffusion, 45, 56
 Dinas Rock, 227
 Dissociation, 6, 294
 Distillation, 221
 Ditté, 289
 Dolliak, 357
 Dolomite, 227
 Draught for furnaces, 277
 Dry processes, 313
 Ductility, 16
 Dudley, 351, 358
 Duffield, 343
 Duhamel, 63
 Duhem, 296
 Dumas, 60
 Dürre, 192

 ECCLÉS, 74
 Eck, 3
 Economic considerations, 359
 Egleston, 320
 Elasticity, 17
 Electric currents, action of, on molten
 alloys, 80
 furnace, 275
 Electro-deposition, union of metals by, 68
 Electrolytic processes, 315
 Emmons, S. F., 251
 Equations, thermal, 305
 Equilibrium, chemical, 8, 294
 Ercker, 70
 Ermann, 63
 Eutectic alloy, 69
 Everard, 112
 Ewing, 129
 Extensibility, 17

 FABER, DU FAUR, 283
 Faraday, 45, 135
 Fire-bricks, 228
 bridge, 255
 clays, 228
 Flame, 139
 Flintshire furnace, 258
 Fleming, Prof., 83
 Flow of metals, 45, 47
 Flowing furnace, 258
 Fluxes, 204
 Forbes, G., 121
 Fortschaufelungs-of-n, 258
 Fracture, 15
 Freiberg process, 323
 Frémy, 184
 Fritache, 90
 Frue vanner, 349
 Fuel, 138

 Fuel, carbonised, 186
 dried, 186
 gaseous, 198
 liquid, 184
 natural, 178
 prepared, 186
 testing of, 292
 Furnace charges, 210
 Furnaces, 227
 Almaden, 269
 Belgian zinc, 268
 blast, 240
 dimensions of, 248
 Brückner cylinder, 266
 calcination, 256
 Catalan, 237
 classification of, 230
 closed vessel, 230, 267
 distribution of charge in, 249
 electrical, 230
 hearths, 230, 233
 Pils, 253, 333
 Raschette, 251
 ratio of parts of, 233
 regenerative, 262
 reverberatory, 230, 255, 258
 shaft, 230, 237
 Fusibility, 42
 Fusible metal, 67
 Fusion, union of metals by, 64

 GANGUE, 204
 Gannister, 227
 Garrison, F. L., 274, 351, 357
 Gaseous fuel, 198
 Gas, natural, 185
 producers, 199
 Gauguin, 86
 Gautier, F., 33
 Geber, 3, 4, 12, 143, 178
 Gellert, 61, 113
 Gérardin, 81
 Gerstenhöfer furnace, 265, 352
 Gilbert, 130
 Gilchrist, P. C., 272
 Gill, T., 111
 Gjer's kiln, 237
 Gmelin, 94
 Godin, 363
 Gold alloys, 100, 101, 107, 170-8
 influence of impurities on, 94
 latent heat of fusion of, 172
 lowering of freezing point, 172
 smelting ores of, 320
 specific heat of, 171
 Gollner's testing machine, 25
 Gore, 86, 121
 Gowland, 71, 101

Wraham, 54, 115
 Greenwood, 74
 Greenwood's testing machine, 25
 Groesclaude, 209
 Gruner, 182, 257, 272, 281
 Guillemin, 353, 358
 Guthrie, F., 45, 69, 118, 137

HADFIELD, R. A., 30, 33, 37, 125
 Harbord, F. W., 37
 Hardening, 108
 Hardness, 16
 Hasenclever furnace, 265
 Hatchett, 60, 89, 94
 Head, J., 262
 Hearths, 233
 Heats of combination, 304
 of isomeric change, 305
 Helmholtz, 53
 Hempel, 117
 Henckel, 113
 Herbert, G., 178
 Heycock, 46, 175
 History of alloys, 60
 of hardening steel, 110
 of metallurgy, 2
 Hochstatter-Godfrey, 102
 Hockin, 86
 Hoffmann kiln, 235
 Holtzer's projectiles, 135
 Homberg, 55
 Hooke's law, 18
 Hopkinson, L., 34, 128, 129
 Hot blast stoves, 282
 comparison of, 287
 Howe, H. M., 28, 30, 137, 168, 358

IGNITION, temperature of, 139
 Iron, allotropic, 98
 carbide of, 117
 carburisation of, 114, 115
 electro-deposited, 28
 hot blast stoves, 282
 influence of other elements on, 27,
 98, 129, 135
 magnetic properties, modified by
 temperature, 129
 impurity, 129
 molecular weakness in, 127
 production of, 367
 thermal treatment of, 108

JAMISON coke oven, 195
 Japanese art metal work, 101
 Jarolimek, 112
 Jars, 70
 Jenkins, 216

Joly, 176
 Joule, 14, 90, 120
 Jullien, 120

KALISCHER, 101
 Karsten, 117
 Kelvin, Lord, 48, 93
 Kennedy, 18, 22, 25
 Kenward, 364
 Kerpelly, 192
 Kilns, 234
 cooking in, 189
 Gjers, 237
 Hoffman, 235
 Styrian, 239
 Kirkaldy, 22
 Kirwan, 114
 Koga, 72
 Kopp, 2

LABORATORY work, 348
 Labour, 359
 Lalonde, de, 268
 Landolt, 57
 Langen, 249
 Laplace, 114
 Laurie, 86, 176
 Lavoisier, 5, 114
 Lead alloys, 107
 sonorous, 47
 oxidation of, 2, 295
 Leadville furnace, 251
 Le Chatelier, A., 21
 Le Chatelier, H., 82, 122, 150, 153, 159,
 295
 Ledebur, 100, 118, 281
 Lemery, 4, 47, 88, 111
 Lencauxes, 74
 Le Play, 320
 Leroy-Beaulieu, 363
 Level, 68, 70
 Lieberkühn's mirror, 353
 Lignite, 180
 Limit of elasticity, 18
 Linde, 86
 Liquefaction, 68, 220
 Liquid fuels, 184
 Lisbonne, 112
 Lockyer, 137
 Lodge, O. J., 82, 85
 B. W., 250
 Longmaid process, 341
 Lüdeking, 15
 Lully, Raymond, 119
 Lupton, 60
 Lürmann, 287
 coke oven, 197

- MACQUEE**, 113
Magnesite, 227
Magnetic properties, 44
Magnus, 120
Mahler, 291
Maitland, 21, 74, 131
Malcolmson, S. W., 339
Malleability, 16
Mallet, 14, 38
Manganese bronze, 105
 steel, 129
 influence of, on iron,
Manhès process, 275
Marguerite, 115
Marten's, Prof., 351, 357
Matthey, E., 73
Matthiessen, 63, 85, 87
Maxwell, 128, 133
Mayer, J. R., 5
Mayo, J., 4
Mazetto, 92
M'Dermott, 343
Mears, 343
Meilers, 187
Melting-points, table of, 153
Mendeleëff, 94, 304
Mercklein, 70
Mercury, price of, 370
Merget, 56
Mesuré's pyrometer, 163
Metals, price of, 368
Metallurgical agents, 205
Metallurgical process, production of, 367
Meunier, 280
Meyer, Lothar, 13, 57, 94, 95, 294
Microscope, use of, in metallurgy, 117
 preparation of specimens, 352
Microstructure of metals, 351
Modulus, elasticity of, 18
Mohr, 64, 66
Moissan, 91, 276
Mokumé, 103
Molecular structure of metals, 13, 87,
 125, 136
Monge, 114
Morveau, G. de, 112, 115
Mouret, 295
Moutier, 297
Müller, 55
Muschenbroek, 61

NATURAL GAS, 185
Natchet's prism, 353
Neilson, 283
Nernst, 289
Neville, 46, 175, 176
Newall, 121
Newlands, 94

Newmann, 113
Nicholson, 109
Nickel, influence of, on iron, 35
 production of, 369
 extraction of, 344
Nies, 15
Noble, 131
Norris, 121

OBACH, 81
Occlusion of gases, 54
Odling, W., 5
O'Hara furnace, 267
Ore-hearth, 234
Ores, 204
Osmond, 19, 99, 122, 351, 356, 357
Ostwald, 177, 289
Oxidation of lead, 2, 295
Oxidising agents, 223

PARACELSUS, 3
Parkes process, 327
Parry, 247
Pattinson process, 314, 327, 337
Pearce, R., 321
Peat, 179
Péclet, 280
Peligot, 72
Pennsylvania anthracite, 183
Pensioners, 360
Pepys, W. H., 116, 136
Percy, J., 1, 27, 182, 320, 323
Permanent set, 18
Pernolet coke oven, 195
Person, 63
Petroleum, 185
Pettus, Sir J., 60
Phillips, 187
Phlogiston, 4, 112
Phosphor bronze, 105
Phosphorus, influence of, on iron, 30
Physical constants of metals, 58
Piecework, 362
Pils furnace, 254, 333
Pionchon, 122
Pistol-pipe stove, 283
Platinum, preparation of, 344
Plattner's process, 7, 342
Playfair, L., 90
Pliny, 110
Plumbago crucibles, 230
Pouff, P., 262
Pouillet, 43
Premiums to workmen, 363
Price of metals, 368
Processes, classification of, 220, 313
 typical, 313

- Producers, 199
 Production of metals, 357
 Profit sharing, 363
 Proust, 89
 Puddling furnace, 255, 258
 Pyrometry, 142
 classification of methods, 144
 Pyrometers, autographic, 151
 Baly & Chorley, 143
 Barus', 156
 calibration of, 152
 Callender's, 149, 158
 Carnelly & Burton, 145
 Crova, 160
 Deville & Troost, 154
 Le Chatelier, 159
 Nouel & Mesure, 163
 Siemens, 147
 Tait, 150
 Wedgwood's, 143
 Weinhold, 143
 Wiborgh, 158
- RAMSAY, W., 47
 Rankine, 140
 Raoult, 46
 Raschette furnace, 251
 Réaumur, 44, 61, 112
 Recalescence, 121, 123, 127
 Redgrave, G., 210
 Reducing agents, 224
 Reduction, 221
 Redshort, 16
 Refractory materials, 227
 Regelation, 53
 Regenerative furnace, 260, 263
 Regnard, 55
 Regnault, 86
 Reiser, 136
 Reuven, 2
 Reverberatory furnaces, 230, 255, 258
 Rey, J., 4
 Reynolds, 48
 Richards, R. H., 249, 349
 Riche, 108
 Riemsdijk, 46
 Riley, J., 35
 Rinman, 113
 Rivot, 320
 Roasting, 7
 Robb, 86
 Robert converter, 274
 Roberts-Austen, 15, 28, 70, 82, 85, 94,
 142, 150, 152, 169, 280
 Root's blower, 282
 Rose, T. K., 46
 Rossignol, 2
 Roessler and Endleman, 296
- Rotzkolk, 186
 Rowan, 200
 Rudberg, 63
 Rumford, 140
- SCHNEURER-KESTNER, 141, 230
 Schild, 357
 Schliemann, 3
 Schützenberger, 90
 Segregation in ingots, 73
 Selection of fluxes, 206
 Shaft-furnaces, 237
 Shaku-do, 101
 Shibu-ichi, 101
 Siemens, Sir W., 260
 F., 262
 furnace, 262
 producer, 199, 262
 pyrometer, 147
 Silicates, 206
 Silicon bronze, 105
 influence of, on iron, 31
 Silver, cost of, 371
 ores, smelting of, 320
 Simon, H., 193
 Simon, Jules, 365
 Simon-Carrès oven, 194
 Slags, 206
 application of, 208
 slag wool, 209
 Snelus, 73, 229, 272
 Solutions, metallic, 75
 Sorby, 117, 351, 356
 Specific extension, 18 *Heat of Metals 58*
 Spencer, J. W., 132
 Spring, Prof. W., 14, 63, 65, 92, 128
 Stack, 277
 Stahl, 5, 112
 Stead, 352
 Steel, classification of, 41, 134
 cooling of, 167
 internal constitution of, 112, 134
 thermal treatment of, 108
 working of, 130
 Stetefeldt furnace, 265
 Stokes, Sir G. G., 75
 Strain, 18
 Strength of metals, 17
 Stress, 18
 Strouhal, 121, 132
 Styrian kiln, 239
 Sublimation, 221
 Sulphur, influence of, on steel, 38
 allotropic, 119
 Sulzback, E. de, 3
 Surface tension, 45
 Surfusion, 45
 Svedelius, 187

- TACHEN, O., 4, 111
 Tait, P. G., 121
 Tap-hole, 242
 Taylor, 86
 Teaching metallurgy, methods of, 348
 Technical instruction, 7, 11
 Tempering, 108
 Temperatures, producing luminosity, 43
 of practical operations, 165
 Tenacity, 16
 Tensile strength, 19
 Testing machines, 22
 Theophilus, 110
 Thermal treatment of metals, 108
 equations, 290, 298, 301, 305
 unit, 140
 Thermo-chemistry, 289
 Thomas, S. G., 272
 Thompson, C., 74
 Thomsen, J., 289
 Tillet, 5
 Tin alloys, 106
 influence of, on copper, 3
 plates, price of, 370
 price of, 370
 Tomlinson, 121
 Toughness, 16
 Treaca, 48
 Trismosin, 119
 Trompe, 237
 Troost, 54
 Truran, 251
 Tungsten, influence of, on iron, 34
 Tunner, Von, 272
 Turner, T., 17, 31
 Tyndall, 53

 UNION of metals, by compression, 65
 by electro-deposition, 68
 by fusion, 63
 Unwin, Prof., 18

 VAN DER MONDE, 114
 Van't Hoff, 177, 294
 Vaporisation, 45
 Vapour pressure, 47
 Violle, 160, 170
 Virchow, 60, 61
 Vivian, Sir H., 94, 320
 Volatility of metals, 56
 Von Hoff, 249

 WAGES, payment of, 362
 Walsh, 247
 Water-gas, 202
 Webb, 135
 Wedding, Prof., 351, 357, 358
 Weinhold, 143, 145
 Welding, 43
 Welsh method of copper smelting, 316
 Werder testing machine, 23
 Werth, 122, 352, 356
 Wet processes, 314
 for argentiferous copper ores, 340
 for nickel ores, 345
 Wheatstone, Sir C., 86
 Whitwell hot-blast stove, 284
 Wicksteed's testing machine, 23
 Williamson, Dr., 366
 Wilson, Oarus, 20
 Wilson gas producer, 200
 Wingham, A., 34, 220
 Winkelmann, 15
 Wood as fuel, 178
 Wright, Dr. Alder, 72, 74, 80, 245
 Wrightson, T., 15, 121

 ZINC alloys, 107
 extraction, 268
 Ziervogel's process, 7, 315, 322
 Zincken, 181

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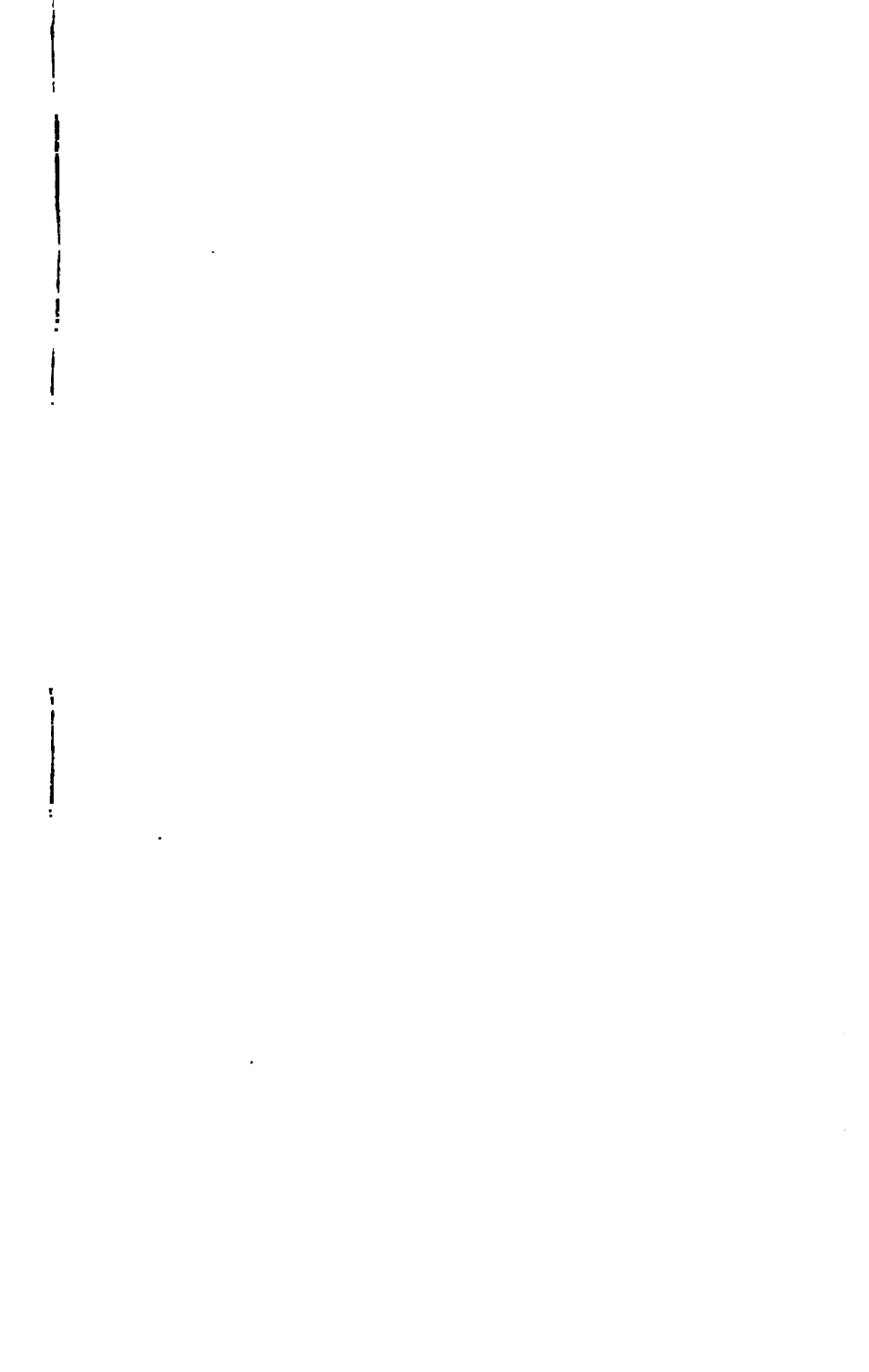
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